ABSTRACT

Title of Thesis: HIGH PRESSURE EMULSION AND MINIEMULSION COPOLYMERIZATION OF VINYL ACETATE AND ETHYLENE

Manu Narayanan
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Thesis Directed By: Professor Kyu Yong Choi, Department of Chemical and Biomolecular Engineering

Miniemulsion copolymerization in gas-liquid systems such as vinyl acetate-ethylene (VAE) differs from that of conventional VAE emulsion copolymerization. Particle nucleation in miniemulsions is mainly due to the radical entry into the monomer droplets. The objective of this thesis is to study the reaction mechanism of VAE miniemulsion copolymerization, characterize the copolymer formed and compare it to the conventionally and commercially used VAE emulsion copolymer, and highlight any advantages of VAE miniemulsions over normal VAE emulsions. Miniemulsions have shown to be more stable and long-lasting than emulsions in terms of particle size distributions. The amount of ethylene incorporated in the copolymer is higher in the case of miniemulsions as compared to emulsions due to decreased mass transfer limitations of ethylene in the aqueous phase and subsequent incorporation into the VAE copolymer.

HIGH PRESSURE EMULSION AND MINIEMULSION COPOLYMERIZATION OF VINYL ACETATE AND ETHYLENE

by

Manu Narayanan

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Advisory Committee:
Professor Kyu Yong Choi, Chair
Professor Amy Karlsson
Professor Dongxia Liu

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LIST OF ABBREVIATIONS

VAc – Vinyl acetate

Eth – Ethylene

HPR – High pressure reactor

LPR – Low pressure reactor

VAE – Vinyl acetate-ethylene

PSD – Particle size distribution

DLS – Dynamic light scattering

^{1}H NMR – Proton nuclear magnetic spectroscopy

I/M – Initiator to monomer molar ratio

S/M – Surfactant to monomer molar ratio

CHAPTER 1

INTRODUCTION

1.1. Background

An emulsion is a dispersion of one immiscible liquid within a second liquid. Depending on the component that gets dispersed in other, they are classified as oil-in-water (O/W) or water-in-oil (W/O) emulsions. Emulsion polymerization is a type of free radical polymerization which involves the formation of a stable emulsion of monomer in water using surfactants. In an oil-water emulsion, monomer droplets in the oil phase are emulsified with the aqueous phase with the help of surfactants. Instead of taking place within emulsion droplets, polymerization takes place in latex particles that form as soon as polymerization initiates [2]. These latex particles grow to about 100 nm in size and they comprise of growing polymer chains. A typical emulsion polymerization formulation comprises of four basic ingredients: monomer, dispersion medium (water), water soluble initiator and emulsifier. When more than one monomer is used, the process that takes place is emulsion copolymerization. The monomer or a mixture of monomers is emulsified in the presence of an aqueous solution of an emulsifier in a suitable container. The monomer is thus present almost entirely as emulsion droplets dispersed in water. Within a certain temperature range, the initiator generates free radicals which in turn initiate polymerization. A stable colloidal dispersion of polymer particles in an aqueous medium must be maintained during the polymerization.

A conventional emulsion polymerization can be divided into three time periods [2]. During the first period, particle nucleation occurs when most of the monomers are located in relatively large monomer droplets of sizes 1–10 μm. Particle nucleation takes place when free radicals formed in the aqueous phase diffuse into micelles and grow via propagation. Polymerization occurs in the aqueous phase to form low molecular weight oligomers that precipitate and become latex particles. Due to the small total surface area of the large monomer droplets, significant nucleation of particles in monomer droplets can be ignored [2]. It is during the second period that polymerization within the monomer-swollen polymer particles occurs with monomers supplied by diffusion from the monomer droplets through the aqueous phase. The third period of emulsion begins when the monomer droplets disappear, or at least reach a polymer fraction similar to that of the particles, and continues to the end of the reaction. For monomers with very low water solubility, the mass transport from the monomer droplets to the polymerization loci can be a critical process.

Miniemulsion polymerization is a special case of emulsion polymerization that involves the use of an effective surfactant/co-surfactant system to produce very small (0.01–0.5 mm) monomer droplets [3]. The monomer droplet specific surface area in miniemulsion system is much larger than those in the conventional emulsion, thus most of the surfactant is adsorbed to the monomer droplet surface, leaving no micelles, and little surfactant to stabilize newly-formed primary particles [4]. Particle nucleation is mainly due to the radical (primary or oligomeric) entry into the monomer droplets

(droplet nucleation). The reaction then proceeds by polymerization of the monomer in these small droplets. Monomer transport through the aqueous phase is not relevant in miniemulsion polymerization, thus monomers with very low water solubility (i.e., ethylene) can be effectively incorporated, as opposed to conventional emulsion polymerization [2].

The surfactant used can have a crucial effect on the conversion, particle size & distribution, viscosity and the overall latex stability of the copolymer. The primary role of surfactant in emulsion polymerization is to lower the interfacial tension, which allows the emulsification of reactive monomers and the formation of stable dispersion of polymer particles [5]. Conventional surfactants aid in the emulsification of monomers inside the micelles, stabilize the polymer particles during nucleation and growth and promote the stability of the resulting latex. Anionic surfactants are known to be strong particle generators and stabilize the latex particles via electrostatic repulsion mechanism [6]. Sodium dodecyl sulfate (SDS) has been used as the anionic surfactant in this study. The concentrations of SDS used are well above the critical micellar concentration (CMC). Typically, the concentration of SDS used would be around 0.5 to 3% of the monomer amount by weight [7].

Vinyl acetate–ethylene (VAE) emulsion is produced by copolymerization of vinyl acetate and ethylene under high pressure; usually, the vinyl acetate content ranges from 60 to 95%, and ethylene from 5 to 40% of the total formulation [8]. The solubilization of ethylene and its mobility to micelles and growing polymer chains depends on physical

parameters such as pressure, reaction temperature and agitation rate. Figure 1.1 depicts the molecular structure of vinyl acetate-ethylene copolymer.

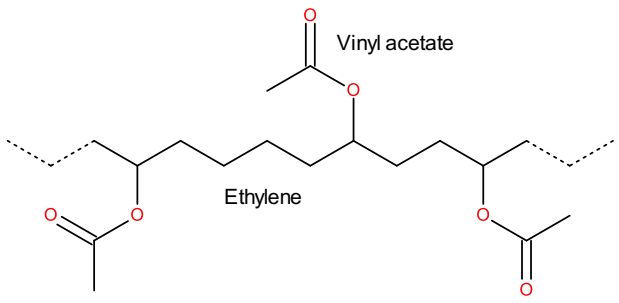


Figure 1.1. Molecular structure of vinyl acetate-ethylene copolymer

When it comes to the production of vinyl acetate-ethylene (VAE) copolymer, the brittle nature of poly-vinyl acetate (pVAc) homo-polymer necessitates its softening by other monomers through copolymerization reactions [9]. Among these monomers, ethylene which is produced in large scale in petrochemical industry has been used extensively. Ethylene has many advantages, since it is inexpensive and offers good mechanical properties to poly(vinyl acetate). VAE adhesives offer appreciable machining properties to p-VAc with the benefit of significantly enhanced adhesion to surfaces that are not porous. Because of their moisture resistance, flexibility, and superior substrate adhesion, VAE emulsions also find applications in adhesives for furniture manufacture, bookbinding and textiles [10]. VAE glues also exhibit better flexibility, water resistance,

and cost-performance while offering superior adhesive binding properties along with more user-friendly compounding characteristics [11]. Laminating applications represent another substantial use for VAE adhesive glue [12]. Flexible packaging adhesives constitute the largest area of application for VAE emulsions including case and carton sealing, bonding of coated board and even in the packaging of foods [13]. VAE emulsions are also popular in the fabrication of non-woven products, such as toweling and diapers, and in the backing of fabrics and carpeting [14].

The properties of VAE copolymer depend largely on the amount of ethylene in the copolymer. It has been shown that higher the concentration of ethylene in the copolymer, lower is its glass transition temperature [15]. Incorporating a higher amount of ethylene in the copolymer is challenging owing to its extremely low water solubility as compared to vinyl acetate [xxx data series]. Due to this reason, ethylene incorporation is governed by the highly limited mass transfer of ethylene from the gas phase to the polymerization loci (polymer particles). The effect of pressure on the ethylene incorporation has also been studied [16]. It has been shown that on comparing two reactions which were run at different pressures keeping all the other conditions constant, as the pressure increased, ethylene percent and molecular weight (M_n) of copolymer increased. In this study, emulsion copolymerization of vinyl acetate and ethylene is reported. The incorporation of other highly water-insoluble monomers via miniemulsion polymerization has been previously successfully demonstrated [18]. Although the conventional emulsion process

of VAE has been extensively studied and even practiced commercially [19, 20], there have been no reports on modeling the production of VAE through a miniemulsion process.

1.2. Objectives and Motivation

Many properties such as glass transition temperature and water resistance of coatings prepared from VAc emulsion polymers can be significantly improved if very hydrophobic monomers like ethylene are incorporated into the polymer backbone [17]. During the nucleation phase of polymerization, polymer particles undergo substantial growth by polymerization. It becomes necessary for the comonomers (VAc and Eth) required for the polymerization to be transported via diffusion through the aqueous phase. However, mass transfer of these monomers from monomer droplets to polymer particles through the aqueous phase is controlled by diffusion, and therefore cannot be readily incorporated into the polymer in conventional emulsion polymerization. It becomes all the more difficult for sparingly water soluble monomers like ethylene to diffuse through the aqueous phase. This represents a limitation of the conventional emulsion polymerization and also a motivation to research on alternate methods of ethylene incorporation. The need of mass transport of monomer through the aqueous phase would be greatly diminished if all or at least a large fraction of the monomer droplets were nucleated. Prevalent droplet nucleation can only occur if the surface area of the monomer droplets is large compared with that of the micelles, and this requires submicron particle size. Miniemulsion copolymerization achieves this target since particle formation takes place primarily via droplet nucleation. The goal of this study is to model

the process of ethylene incorporation in the VAE emulsion and miniemulsion polymerization technique at low and high ethylene pressures, and to also study the stability, properties and differences, if not advantages, of a VAE latex generated by miniemulsion copolymerization as compared to that generated via normal conventional emulsion copolymerization.

Chapter 2 presents a review of literature needed to have a thorough understanding of the topic and identify similar work done within the area. Chapter 3 outlines a brief description of the materials used in the study and the analytical techniques and methods employed. Chapters 4, 5 and 6 describe in detail all the results obtained as part of emulsion and miniemulsion VAc homo-polymerization, VAE emulsion copolymerization and VAE miniemulsion copolymerization respectively. The study is summarized and concluded in Chapter 7. A catalogue of all the ^{1}H NMR spectra is provided as part of Appendices A and B, followed by relevant references.

CHAPTER 2

LITERATURE REVIEW

A wide range of synthetic polymeric materials like paints and coatings are commercially produced by emulsion polymerization [21]. VAE emulsions have been developed with excellent properties for use in paints, coatings, cement modifiers, adhesives, and paper processing [17]. VAE should not be confused with EVA copolymers, for the vinyl acetate content of EVA is below 40% while that for VAE is at least 50% [2]. The following is a review from available literature on components of an emulsion and their effects on the emulsion properties, various stages of emulsion and miniemulsion polymerization and kinetics of free radical copolymerization.

2.1. Components of an emulsion

A typical emulsion formulation includes water, surfactant, initiator, a mixture of monomers and additionally a co-surfactant in the case of miniemulsions. Co-surfactants are ideally water-insoluble and monomer-soluble which help to further reduce diffusional degradation, interfacial tension and Ostwald ripening of submicron droplets [22].

2.1.1. Effect of surfactant type and concentration

Surfactants help to reduce the interfacial tension between the monomer (oil) phase and the aqueous phase by dispersing or emulsifying the monomer in the water phase via agitation. When surfactants are used at concentrations exceeding the critical

micelle concentration (CMC), they form micelles which are emulsifier molecules clustered in an orderly manner, such that the hydrophobic part of the molecule orients itself towards the center of the cluster while the hydrophilic part of the molecule orients itself towards water. They help dissolve the monomer within emulsifier molecules, stabilize the droplets, growing latex particles, particles of the final latex and the polymer particles in a dispersed emulsion form. Surfactants also play a key role in serving as the site for the nucleation of particles and as chain transfer agents. The effects of different colloidal stabilizers on vinyl-acetate copolymer emulsions and films have been studied [9]. In general, anionic emulsifiers are extensively preferred in many emulsion polymerization systems. They serve as strong particle generators and stabilize the latex particles via electrostatic repulsion mechanism. Examples of anionic emulsifiers include cetyl trimethyl ammonium bromide (CTAB), lauryl dimethyl amine oxide, sodium dodecyl sulfate (SDS). SDS has been used as the anionic surfactant in this study.

2.1.2. Effect of initiator

The type of initiator and its concentration has a significant effect on the number of initiating species or free radicals and as a result, many properties of the copolymer concerning stability such as particle size, distribution, and average molecular weight are affected [23]. The rate of initiation is plays a significant role in obtaining monodisperse polymer particles during emulsion polymerization processes. Selection of a suitable initiator for a system is a crucial factor for a successful emulsion and miniemulsion polymerization because an initiator should be chosen in such a way that it does not

decompose prematurely at a low temperature during the starting stages of polymerization as it can lead to a low conversion and a broad particle size distribution. Most of the initiators such as benzoyl peroxide (BPO), lauroyl peroxide (LPO), and azobisisobutyronitrile (AIBN) decompose at temperatures well above 50°C. Potassium persulfate is another initiator used whose decomposition temperature lies in the range of 50-60°C, and decomposes at a rate of 6.9 x 10^{-5} s^{-1} at 60°C [24]. KPS has been used as the initiator system in the study where the experimental runs are carried out at 60°C. The rate of polymerization depends on the concentration of free radicals. The initiator concentration has a significant effect on the concentration of free radicals during the initial stages when the conversion is not very high. Hence, an increase in the initiator concentration brings about an increase in the rate of polymerization. The rate of polymerization, however, becomes independent of the initiator concentration at higher conversions. At these conversion levels, the reaction primarily proceeds through a heterogeneous mechanism in the particle phase. Such a process does not involve the formation of any new polymer chains and would be therefore, expected to be independent of the solution phase initiator concentration.

2.1.3. Effect of agitation

The stirring speed has a paramount effect on the particle formation in emulsion and miniemulsion polymerization processes. Increasing the agitation ensures thorough mixing and an increase in the polymerization rate. A high stirring speed as an effect on the mass transfer rates of radicals and monomer. A thorough mixing enables the ethylene

molecules to reach the monomer sites in emulsions and growing polymer particles in miniemulsion VAE copolymerization. An increase in the agitation rate usually results in a decrease in the mean particle size and average molecular weight. The particle sizes decrease because an increase in the rate of agitation would correspond to an increase in the shear force, which causes the particle sizes to decrease [25]. The average molecular weight usually decreases when the agitation speed increases because at a higher agitation rate, the shearing force overcomes the solution viscosity to induce faster chain diffusion in the polymer solution. Because of this, the rate of the chain termination is higher, thereby yielding polymers with the lower molecular weights [26]. A high stirring speed also results in a higher rate of particle aggregation due to the shear stress of the fluid [27].

2.1.4. Effect of inert gas purging

Studies have shown that purging the reaction media with nitrogen decreases the polydispersity of polymer particles in emulsion polymerization. A possible explanation for the effect of the purging with nitrogen is based on the nucleation stage. Initially, the system is a homogeneous solution where radicals are produced by decomposition of the initiator. These radicals react with monomer to form polymer chains. The oxygen acts as an inhibitor because it reacts rapidly with free radicals and reduces the concentration of free radicals and, hence, the nucleation rate will decrease. This will make the nucleation period longer, resulting in a broad particle size distribution. It should be noted that oxygen is not completely dissolved in the medium so the diffusion of the oxygen from the headspace of the polymerization container to the reaction mixture during the

polymerization process leads to a continuous partial inhibition that makes polydisperse polymer particles [28,29].

2.2. Stages of Emulsion Polymerization

Emulsion polymerization is initiated by the addition of an initiator. According to the theories proposed by Smith and Ewart [30], conventional emulsion polymerization mechanism comprises of three intervals: (a) initial (particle formation or nucleation) stage, (b) particle growth stage and (c) the completion stage.

Initial particle nucleation stage (Interval I): With the addition of initiator to the reaction mixture, the free-radicals which are generated in the aqueous phase diffuse into the monomer-swollen micelles and initiate the These micelles are the primary loci for the formation of polymer particle nuclei. These are the sites where the water-soluble initiator interacts with the hydrophobic monomer. These exhibit an extremely large oil-water interfacial area for diffusing of free-radicals and have high monomer concentration. After nucleation, monomer-swollen micelles are transformed into polymer particles swollen with monomer. As the monomer gets consumed with in the reaction loci by the polymerization process, other monomer molecules are then absorbed into the particles continuously from monomer droplets by diffusion through the aqueous phase. Thus, the micelles grow from tiny groups of emulsifier and monomer molecules to larger groups of polymer molecules held in emulsion by the action of the emulsifier molecules located on the exterior surfaces of the particles. With the continued adsorption of micellar emulsifiers on to growing particles, the micelles begin to disappear. The particle

nucleation stage (Interval I) ends with this disappearance of the micelles at a relatively early stage in the reaction (around 10-20% conversion).

Particle growth stage (Interval II): Upon completion of the particle nucleation process, polymerization proceeds homogeneously in the polymer particles as the monomer concentration in the particles is maintained at a constant value by diffusion of monomer from the monomer droplets into the polymer loci. The rate of polymerization in this stage is constant. The monomer droplets decrease in size as the size of the polymeric particles increase. The particle growth stage (interval II) ends when monomer droplets completely disappear in the polymerization system (around 50-80% conversion). The polymer particles now contain most of the unreacted monomer and essentially all the emulsifier molecules attached to their surface.

Completion stage (Interval III): This is the final stage of the reaction where polymerization continues within the monomer-swollen polymer particles formed during Interval I, and persisted and grew through Interval II. In the ideal case, the number of reaction loci during this stage is essentially fixed at the number which had become formed at the end of Interval I. However, the concentration of monomer in the reaction loci and the polymerization rate continues to decrease toward the end of polymerization. The polymerization is finally complete with the system now comprising of a dispersion of small polymer particles stabilized with the molecules of the original emulsifiers.

2.3. Miniemulsions

The stability of mini-emulsions can continue for as little as days to as long as months. Miniemulsions can be generated by dispersing the monomer phase in the aqueous phase by means of ultrasonication or vigorous mechanical agitation (homogenization). A mixed emulsifier system is employed which includes a classical surfactant such as SDS and a water-insoluble co-surfactant such as a long chain fatty alcohol or alkane. Hexadecane is the co-surfactant used in this study. The polymerization of miniemulsions can begin with monomer droplets at submicron sizes ranging from 50 nm to 500 nm [31]. In case of prevailing droplet nucleation or initiation of polymerization in the droplet itself, each miniemulsion droplet can be treated as a small individual reactor. The monomer droplets themselves serve as the nucleation sites for the particles. Therefore, the droplet stability is a crucial factor in order to obtain the necessary droplet nucleation. The better the droplets are stabilized, the higher is the droplet nucleation.

The mechanism of miniemulsion copolymerization is quite similar to that of emulsion polymerization except that it does not go through interval II in the Smith-Evart kinetics. The initiation process becomes more transparent when the rate of polymerization is transferred into the number of active radicals per particle, ñ, which slowly increases and stabilizes to ñ = 0.5 [31]. Since each miniemulsion droplet can be perceived as a separate reactor, it is assumed that the droplets (reactors) do not interact with each other. Thus, the start of the polymerization in each miniemulsion droplet is not simultaneous, and hence conversion in each droplet is probably different. Upon reaching

this mean radical number, the polymerization kinetics starts to slow down again and follows the kinetics of interval III described in Section 2.2. As reasoned by the droplet nucleation mechanism, only the monomer in the droplet is available for polymerization, which gets exponentially depleted from the reaction site as polymerization proceeds and gets completed. Figure 2.1 shows a schematic of (a) VAE emulsion and (b) VAE miniemulsion copolymerization systems. As can be seen, the VAc monomer has to diffuse from the large monomer droplets to the polymerization loci in emulsions while each droplet in the miniemulsion is like an individual reactor that does not have mass transport limitations.

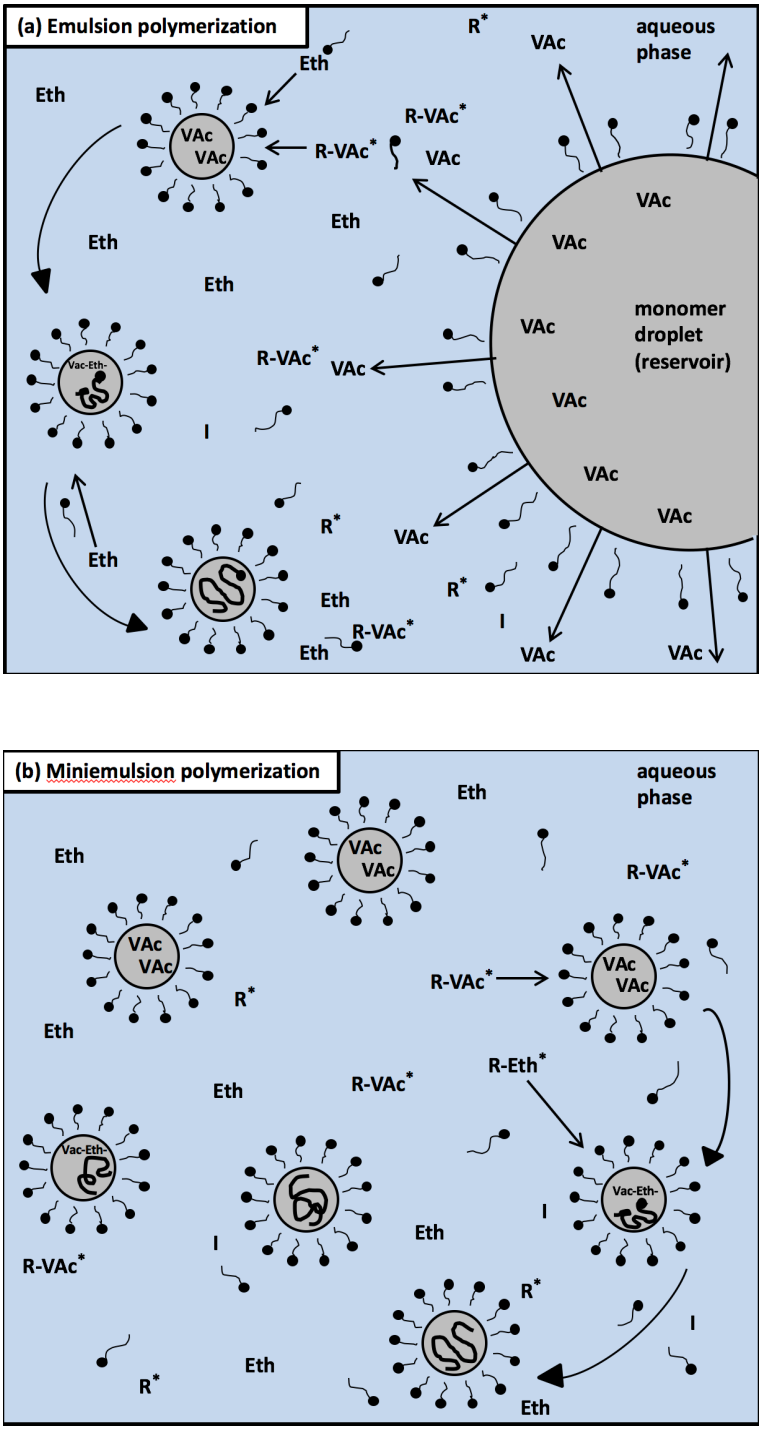


Figure 2.1. Schematic of mechanism of (a) emulsion and (b) miniemulsion polymerization process.

2.4. Particle sizes and Coagulation

Particle size distribution (PSD) is by far the most important characteristic of a monomer miniemulsion because it affects directly both miniemulsion stability as well as droplet nucleation [32]. As described in Section 2.3, each droplet in a miniemulsion is visualized as a reactor. Hence, for polymerization to take place, it is very important for each droplet to be stable against Ostwald ripening, the process where particles from the monomer phase diffuse from smaller to larger droplets through the aqueous phase. The evolution of mean particle size with time is the main parameter to characterize the stability of emulsions and miniemulsions because instability phenomena and particle sizes are directly linked to one another. Coalescence and Ostwald ripening tend to increase the average particle size. Flocculation does not affect the particle size because droplets do not merge. Thus, a clear understanding of the mechanisms involving miniemulsion polymerization strongly depend on the accuracy with which the particles sizes are determined. Dynamic light scattering (DLS) has been used to determine the droplets size of the latex in this study. In this technique, vast dilution is needed to avoid multiple scattering. The dilution is made by using the aqueous phase of the same miniemulsion. Once they are formed, the miniemulsions may be stored for some time until they are polymerized. During this stage, particle size may increase because of degradation of droplets by monomer diffusion. This is often the most important mechanism for the increase in size of the monomer droplets. Particle sizes may also increase because of

coalescence of droplets caused by droplet collision due to Brownian motion and van der Waals forces.

During the time elapsed between miniemulsion preparation and polymerization, the PSD may vary because of coalescence caused by droplet collision due to Brownian motion and van der Waals forces and because of droplet degradation by monomer diffusion [33]. The extent of the coalescence may be greatly reduced by using a good surfactant system. On the other hand, the extent of the droplet degradation by monomer diffusion can be largely minimized by including a co-surfactant in the formulation. It is to be noted that all miniemulsion formulations include the co-surfactant. An important characteristic of the co-surfactant is to modify the thermodynamics involving the partitioning of the monomer, thereby influencing the monomer mass transfer rate. Influencing the monomer mass transfer can play a crucial role in influencing the incorporation of sparingly water soluble co-monomers like ethylene into the VAE copolymer. Thus, the particle size measurement is of great importance as it provides a lot of information about the emulsion properties.

2.5. Kinetics of Free Radical Polymerization

The following scheme is a kinetic mechanism for a typical free radical polymerization initiated by thermal initiators. In heterogeneous polymerizations, these reactions can take place in each of the phases present in the system.

$I \xrightarrow{k_d} 2\dot{R}$ Radical formation (Generation)

$\dot{R} + M \xrightarrow{k_i} \dot{P}_1$ Initiation

$\dot{P}_n + M \xrightarrow{k_p} P_{n+1}^{\cdot}$ Propagation (for n ≥ 1)

$\dot{P}_n + X \xrightarrow{k_{fs}} M_n + \dot{X}$ Chain transfer

$\dot{P}_n + \dot{P_m} \xrightarrow{k_{tc}} M_{n+m}$ Chain termination by radical coupling (combination)

$\dot{P}_n + \dot{P_m} \xrightarrow{k_{td}} M_n + M_m$ Chain termination by disproportionation (β - hydrogen transfer)

where I = initiator, $R^{\bullet}$ = initiator radical, M = monomer, $P_n^{\bullet}$ = live polymer radical with n monomer units, $X^{\bullet}$ = monomer, chain transfer agent, solvent, polymer, impurity etc. M_n = dead polymer chain with n monomer units (n ≥ 2).

According to this scheme, the polymer chains are initiated by free radicals generated by the attack of initiator radicals to monomer molecules. Initiator radicals can be produced using heat, irradiation, redox systems, etc. Then, the free radicals which are generated from decomposition of initiator, adds to the double bond of the monomer and another radical is produced by the resultant unpaired electron (primary radical). This new radical is then free to react with another monomer unit. The procedure of chain growth continues in this way until the radical is terminated by recombination or

disproportionation when it is transferred to another chain.

In termination by combination, two chains are joined together and their unshared electrons are coupled to form a single bond between them. In termination via disproportionation, there is an abstraction of proton from the penultimate carbon of one chain to the others. The relative proportion of each termination type depends on the reaction temperature and on the particular polymer. For instance, termination reaction for vinyl acetate polymerization over 60°C is disproportionation [34].

2.6. Effect of pressure on ethylene solubility

Figure 2.2 shows a plot of solubility of ethylene in both vinyl acetate and water at 60°C as a function of pressure obtained from the solubility data series [17]. It can be seen that ethylene is almost completely immiscible with water and that ethylene uses water as a carrier to ferry itself to the vinyl acetate monomer droplets or the polymerization loci. The solubility of ethylene in vinyl acetate shows a considerable linear increase with pressure. Since all the experiments had been carried out in a semi-batch manner, it can be assumed that concentration of ethylene in the bulk organic phase remains constant throughout the entire duration of the polymerization. In other words, as the ethylene dissolved in the organic monomer phase (vinyl acetate) gets incorporated into the copolymer, more ethylene from the overhead space moves through the water to dissolve into the organic phase thereby maintaining an equilibrium. Higher the ethylene pressure, higher is the concentration of ethylene around the monomer droplets, and greater is the possibility that a growing polymer chain will accept the ethylene molecule in the vicinity

as opposed to accepting a vinyl acetate molecule.

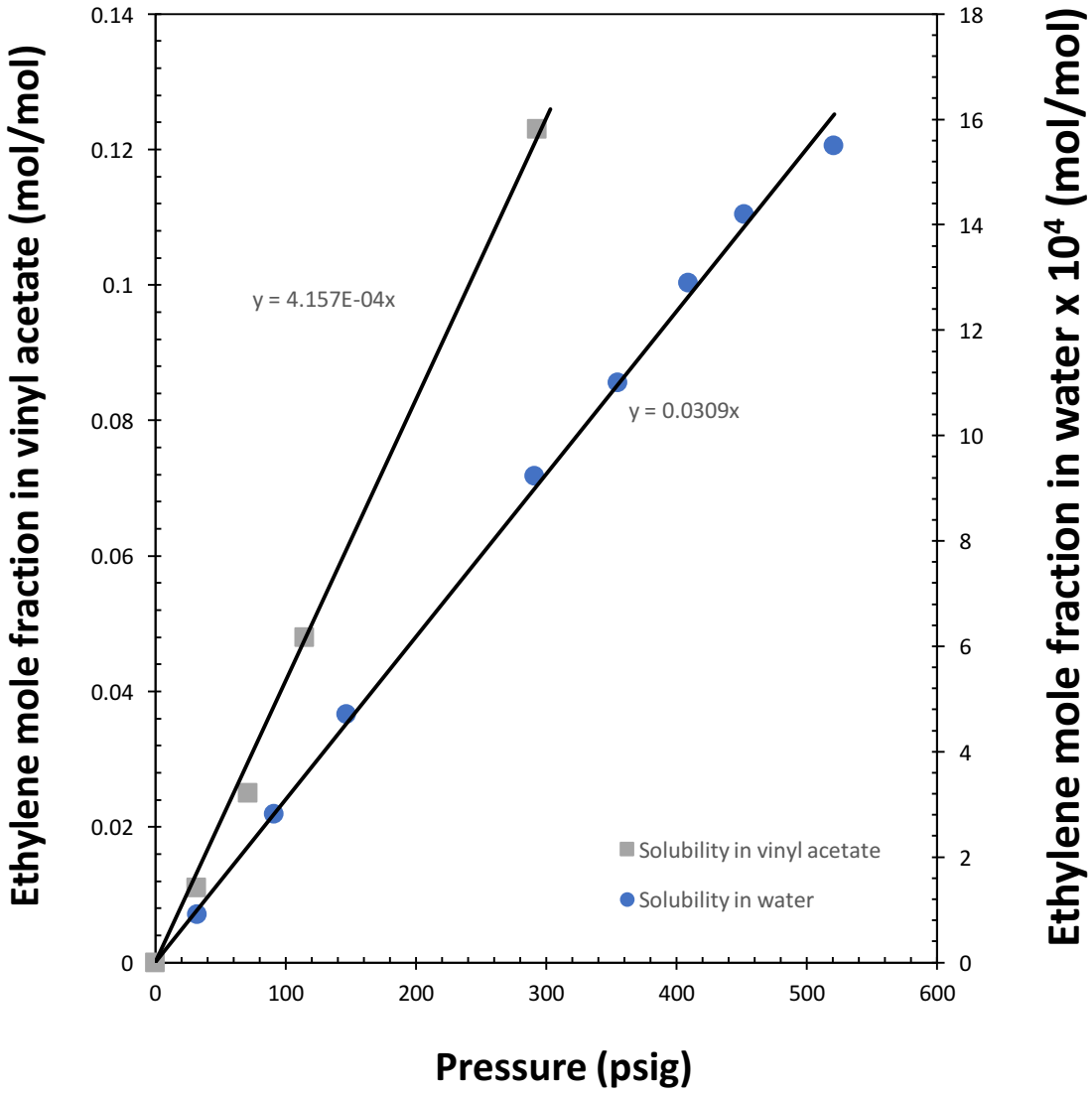


Figure 2.2. Plot of dissolved ethylene mole fraction versus ethylene partial pressure in vinyl acetate and water solvents at 60°C

2.7. Copolymer Equations

During the free radical copolymerization of two co-monomers M_1 and M_2, it is interesting aspect to relate the final copolymer composition with the initial monomer composition in the bulk phase. For the copolymerization of a binary copolymer, four possible propagation reactions can be distinguished. The first two apply to the reactions that can occur if the active site (radical) at the end of the growing chain happens to the monomer of type 1. This can either add to another unit of type 1 with a rate constant given by k_{11}, or a unit of type 2 whose rate constant is given by k_{12}. Similar equations can be written for the addition to a type 2 radical.

$$M_1^* + M_1 \xrightarrow{k_{11}} M_1M_1^*$$

$$M_1^* + M_2 \xrightarrow{k_{12}} M_1M_2^*$$

$$M_2^* + M_2 \xrightarrow{k_{22}} M_2M_2^*$$

$$M_2^* + M_1 \xrightarrow{k_{21}} M_2M_1^*$$

where the reactivity ratios r_1 and r_2 are defined in Equations 2.1 and 2.2.

$$r_1 = \frac{k_{11}}{k_{12}} \qquad (2.1)$$

$$r_2 = \frac{k_{22}}{k_{21}} \qquad (2.2)$$

The bulk composition can be obtained from polymer composition using the Mayo-Lewis

equation [35] that follows.

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \qquad (2.3)$$

where F_1 is the mole fraction of 1 in the copolymer and $F_2 = 1 - F_1$. Figure 2.3 shows a characteristic plot of the relation between F_2 and f_2 for different values of the reactivity ratios r_1 and r_2. The line y = x ($r_1 = r_2 = 1$) has also been plotted for reference. Note that it is a plot of F_2 vs f_2 and not F_1 vs f_1, because the subscript '2' denotes ethylene and that a similar plot of F_2 vs f_2 for ethylene has been plotted in the Chapter 6 which can be compared with Figure 2.3. When $r_1 = r_2 = 1$, it leads to a very special case where monomers 1 and 2 with add with equal specificity to either type of radical active site, M_1 and M_2 radicals. The resulting copolymer not only has a truly random distribution of monomers, but the copolymer composition is exactly same as that of the initial monomer concentration and stays so throughout the course of the polymerization i.e., $F_1 = f_1 = (f_1)_{t=0}$. The instantaneous mole fraction of ethylene in the monomer mixture, f_2 can be calculated based on f_1 as a function of vinyl acetate conversion.

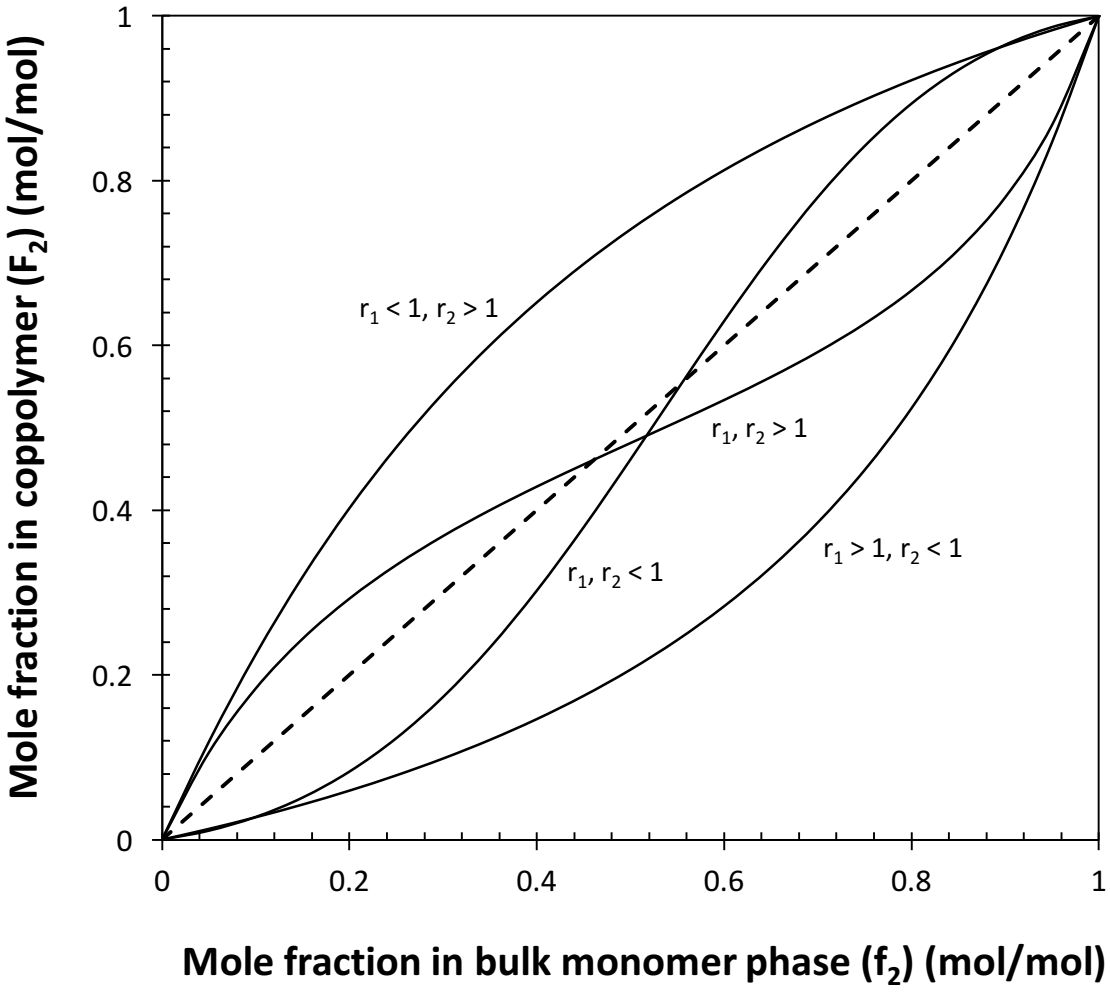


Figure 2.3. Plot of mole fraction in the copolymer as a function of bulk phase mole fraction for different values of r_1 and r_2.

CHAPTER 3

MATERIALS AND METHODS

3.1. Materials

Vinyl acetate (VAc 99+ %), sodium dodecyl sulfate (SDS), potassium persulfate (KPS) and hexadecane (HD) were all purchased from Aldrich and used as received. High pressure ethylene and nitrogen gas was purchased from Airgas. Only deionized water was used in this study.

3.2. Emulsion and Miniemulsion Preparation

Conventional emulsion homo-polymerization of vinyl acetate, conventional and miniemulsion copolymerization of vinyl acetate and ethylene was performed in this study. Emulsions were made using vinyl acetate (oil phase) dispersed in water (aqueous phase) using sodium dodecyl sulfate as the surfactant. Potassium persulfate (KPS) which was used as the initiator for the polymerization was also added to the mix. In the case of vinyl acetate-ethylene copolymerization, ethylene was the other monomer that was pressurized in gaseous phase over the reactor contents. However, in the case of vinyl acetate homo-polymerization, nitrogen was purged into the contents as an inert gas in place of ethylene.

Miniemulsions are made by the application of high shear force on a normal emulsion. Generating a minemulsion from an emulsion was primarily done by

ultrasonication in this study. Emulsions containing the oil phase, aqueous phase, surfactant and the co-surfactant were subjected to high shear using a tip sonicator (Omniruptor 250) at 30 kHz for 14 minutes in all the experiments. This resulted in a stable miniemulsion of particle sizes less than 100 nm before polymerization. Due to the exothermic nature of ultrasonication, it was conducted in an ice water bath. The initiator was added after the process and right before initiation of polymerization. Figure 3.1 (a and b) shows a photograph of the homogenizer and ultrasonicator used in the study.

(a) (b)

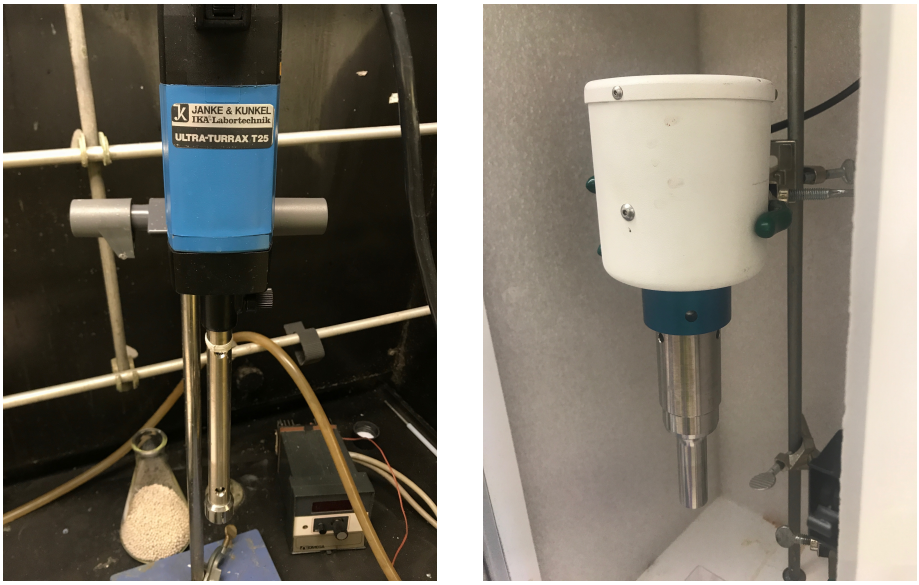


Figure 3.1. Photograph of the (a) homogenizer and (b) ultrasonicator used in the study

3.3. Experimental Setup

3.3.1 Low Pressure Reactor

Experiments were performed on a batch and semibatch basis in a glass reactor (Andrew's Glass Co.) that would allow a maximum pressure of about 100 psig. Figure 3.2 shows a schematic of the low pressure reactor used in the study. Either nitrogen or ethylene gas would flow from their respective gas cylinders into the reactor via three way valves and a pressure gauge that monitors the pressure. The temperature is solely controlled by a heat pad and there is no coolant used in the system. The temperature of both the reactor contents and the water from the water bath is monitored via thermostats. Ethylene was fed as needed to keep the ethylene headspace pressure constant. Additional provisions were made so that samples could be taken out whenever needed during the run so that conversion-time profiles could be studied. The overhead pressure would force the latex through the sampling pipe when the valve is opened. An agitation 400 rpm was maintained with the help of a magnetic stirrer. Figure 3.3 shows the actual photograph of the low pressure glass reactor used in this study.

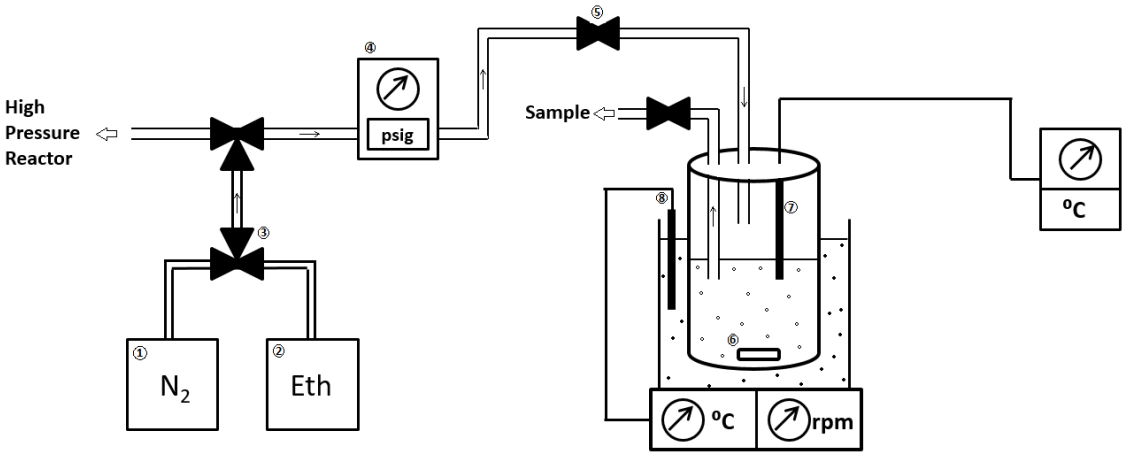


Figure 3.2. Schematic of low pressure reactor used in the study.

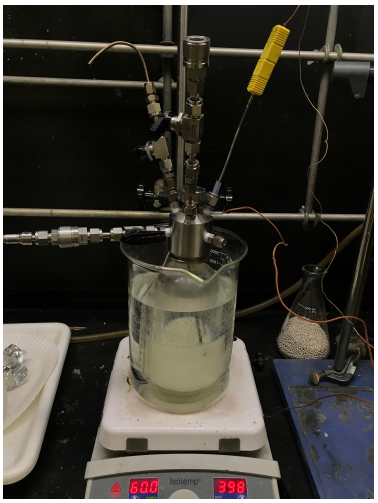


Figure 3.3. Photograph of low pressure reactor used in the study.

3.3.2. High Pressure Reactor

Figure 3.4 shows the schematic of the high pressure reactor used in the study. The system was initially purged with nitrogen gas to create an inert oxygen-free atmosphere following which the inflow of nitrogen gas was changed to that of ethylene using Swagelok® three

way valves. The reactor contents were again purged with ethylene for 5 minutes following which the gas outlet was sealed and the pressure in the reactor was raised to the desired value, as measured by a pressure gauge before the start of the run. The reactants were agitated at 700 rpm and the temperature was maintained at 60°C by Eurotherm 92 temperature control (Autoclave Engineers). This steady maintenance of temperature at 60°C is brought about by a solenoid valve that creates a balance between the heat-supplying high temperature furnace that surrounds the reactor wall and a heat-absorbing coolant jacket that carries water through the reactor. The temperature of the reactor contents was monitored by a thermostat inserted into the reactor. The experimental run was 4 hours long with the timer initiated as and when agitation and the temperature controller was switched on. Unlike the low pressure reactor, the high pressure reactor did not have a provision for taking samples during the run. A snoop solution was used to detect leaks at joints prior to every run. At the end of the run, the gas outlet was slowly opened allowing the ethylene to escape thereby reducing the pressure in the reactor. The synthesized emulsion was then stored and tested for particle size, composition and rheological measurements. Figure 3.5 shows the actual the photograph of the high pressure reactor and Eurotherm 92 temperature control used in this study.

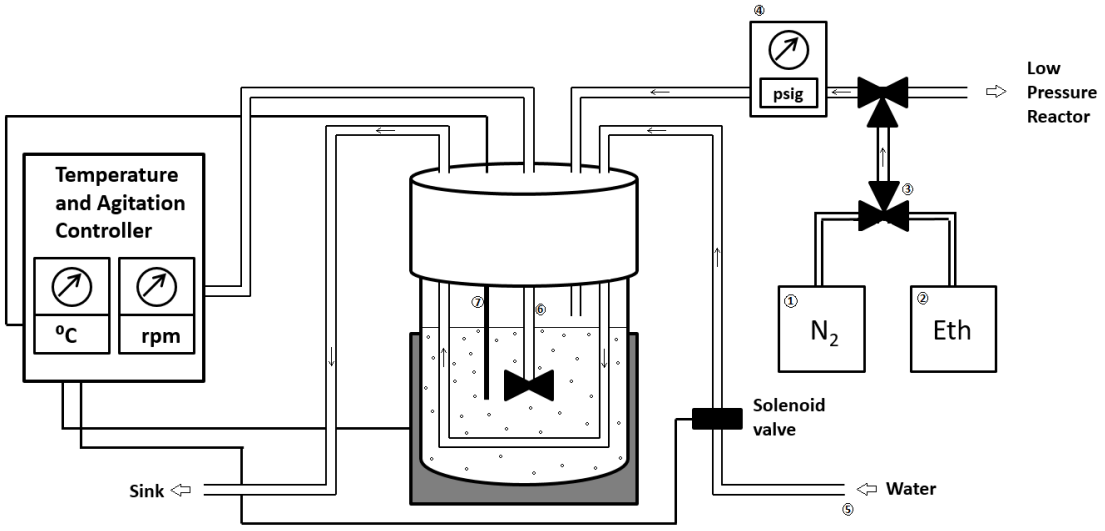


Figure 3.4. Schematic of high pressure reactor used in the study.

(a) (b)

Figure 3.5. Photograph of (a) Eurotherm 92 temperature and agitation controller and (b) high pressure reactor used in this study

3.4. Analytical Techniques

3.4.1. Total solid content (TSC) and conversion

Gravimetric methods were employed in determining the total solids content of a monomer. A small amount of the latex sample was taken from the reactor at different time points and the polymerization was terminated by adding a few drops of methanol. While the wet sample consisted of VAE, SDS, KPS, VAc, water and HD, the dry sample would contain only VAE, SDS and KPS. The weight of SDS and KPS are negligible in comparison to that of VAE, hence can be ignored. Polymer samples whose TSC needs to be measured are weighed before and after drying away the non-solid and non-polymer components in a 37°C oven for 48 hours. Equation 3.1 describes how the TSC is calculated.

$$\mathrm{TSC} = \frac{(\text{Weight of plate+dried latex}) - \text{Weight of plate}}{(\text{Weight of plate+sample}) - \text{Weight of plate}} \qquad (3.1)$$

where TSC can be expressed as a percentage or decimal. Once the composition of the polymer is known, VAc conversion can be calculated by comparing it with the known composition of VAc in the monomer phase before the start of polymerization.

3.4.2. Droplet size

Particle size (diameter) measurements through Dynamic Light Scattering (DLS) were performed on Malvern Zetasizer Nano ZS90 (Malvern Instruments, Southborough, Massachusetts) equipped with a non-invasive back scatter technology. The experiments

were performed in the homodyne mode at 90◦ scattering angle. Polymer emulsion/miniemulsion samples were diluted 1000-fold in deionized water prior to the measurements. After dilution, 1 ml of the sample was placed in a 12 mm square polystyrene cuvette (Malvern Instruments) followed by equilibration to 25°C before the measurement. The first measurement of particle sizes were measured right after the polymerization. Consequent measurements were also done on a weekly basis to monitor the stability of polymers over time. Figure 3.6 shows a photograph of the Malvern Zetasizer Nano ZS90 used in the study.

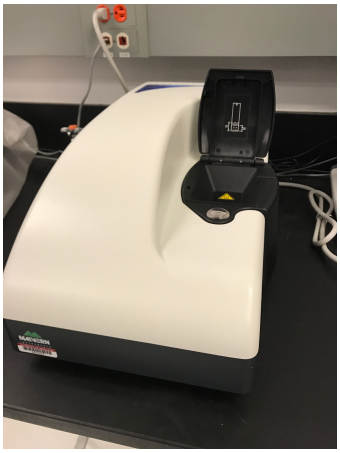


Figure 3.6. Photograph of the Malvern Zetasizer Nano ZS90 used in the study.

3.4.3. Copolymer composition

The composition of ethylene in the copolymer needs to be determined in order to obtain the conversion from the monomers. Copolymer composition was determined using proton ^{1}H proton NMR (Bruker Avance, 400 MHz) using deuterated chloroform

($CDCl_3$) as the solvent. Bruker TopSpin 2.1 was the software used to analyze the spectra. The approximate concentration of the sample used was 5-10 mg of dried latex sample in 1ml of $CDCl_3$. No gel formation was observed during the sample preparation, i.e., the VAE samples were completely dissolved in the $CDCl_3$.

The VAE copolymer composition was obtained using ^{1}H proton NMR. Figure 3.7 shows a sample ^{1}H NMR spectrum. In Figure 3.7, the peak at 4.85 ppm corresponds to the α-H (-CH- in VAc segment); the broad peak from 1.55 to 1.83 ppm represents the β-H (-CH_2- in VAc segment); the CH_3 group of VAc appears as a peak at 2.0 ppm. The CH_2 peak of ethylene segment appears at 1.23 ppm. The peak at 0.86 ppm corresponds to the -CH_3 group derived from H-abstraction by the ethylene -CH_2 radical. Equation 3.2 adapted from Guo et al. [2] is helpful in determining the molar ratio of ethylene to vinyl acetate in the VAE copolymer.

$$Eth{:}VAc = \frac{I_{0.8-2.3ppm} - 5I_{4.9ppm}}{4I_{4.9ppm}} \qquad (3.2)$$

where 'I' represents the integral of a peak in the ^{1}H NMR spectra. Using Equation 3.2, the vinyl acetate-ethylene molar ratio of a sample spectrum shown in Figure 3.7 can be calculated as follows.

$I_{0.8\text{-}2.3ppm}$ = 6.03 + 69.69 + 64.90 + 46.71 + 10.00 = 197.33

$I_{4.9ppm}$ = 24.11

$$Eth:VAc = \frac{197.33-5(24.11)}{4(24.11)} = 0.796$$

Thus the ratio of moles of ethylene to that of vinyl acetate in the copolymer is 0.796. A catalogue of all ^{1}H NMR spectra with their respective peak integral values are provided in Appendices A and B.

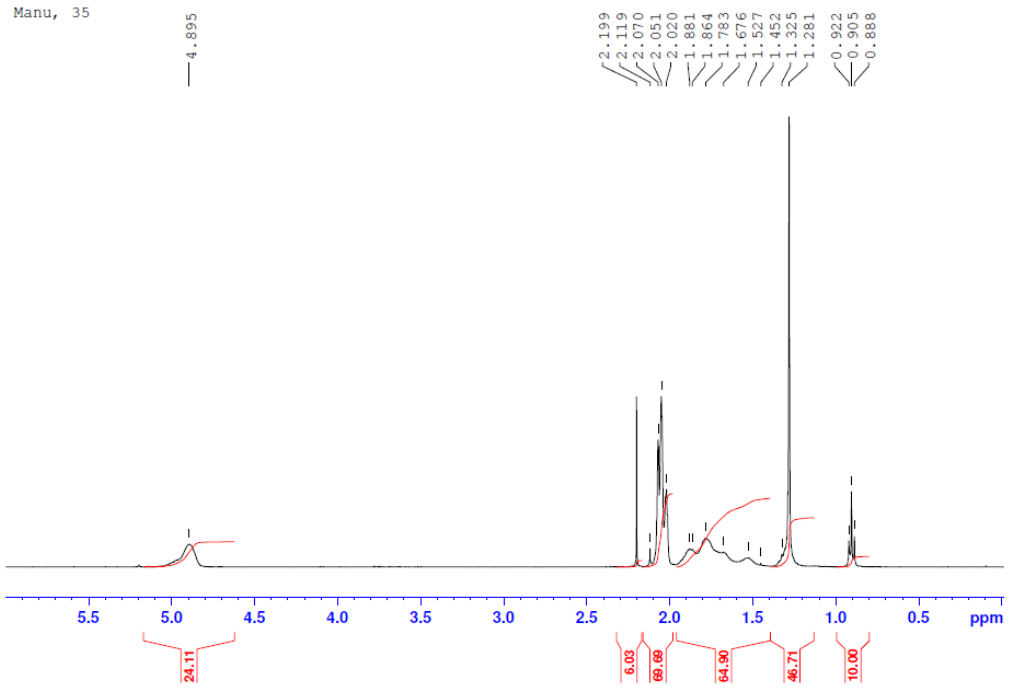


Figure 3.7. Sample ^{1}H NMR spectrum of VAE copolymer

3.4.4. Viscosity

All rheological experiments were performed on TA instruments AR2000 stress-controlled rheometer. Experiments were performed at 25°C utilizing a cone and plate

geometry (60 mm diameter and 2° cone angle). The cone is made of aluminum which has a high coefficient of thermal expansion and is chemically compatible with VAE copolymer and poly-vinyl acetate polymer material. As it is lighter, inertial effects can also be neglected. A larger diameter of 60 mm was ideal for low viscosity samples such as VAE emulsions. Solvent drying was minimized through the use of a solvent trap. Steady shear experiments were performed to determine the apparent viscosity of the sample as a function of shear rate. The value of viscosity of the sample was taken when the viscosity was independent of the changing shear rate. Figure 3.8 shows a photograph of the rheometer and the cone and plate geometry used in the study.

(a)

(b)

Figure 3.8. Photograph of (a) rheometer and (b) cone and plate geometry used in the study

CHAPTER 4

EMULSION AND MINIEMULSION HOMO-POLYMERIZATION OF VINYL ACETATE

4.1. Introduction

The first part of the results is a summary of the preliminary experimental results regarding emulsion and miniemulsion homo-polymerization of vinyl acetate at 60°C. The results have been presented in two parts – conventional vinyl acetate polymerization followed by miniemulsion polymerization of vinyl acetate. The reaction conditions for the experiments involving emulsion copolymerization of vinyl acetate with ethylene are shown in Appendix A.1. The effect of initiator and surfactant concentration on the monomer conversion is studied, followed by a comparison of the conversion-time profiles, particle size distribution and viscosities of miniemulsion and emulsion polymer latexes.

4.2. Vinyl Acetate Emulsion Polymerization

4.2.1. Effect of initiator

Selection of a suitable initiator for a system is a crucial factor for a successful emulsion and miniemulsion polymerization. The initiator used in this study is potassium persulfate (KPS). Varying the ratio of initiator concentration to monomer (I/M) concentration and observing the properties of the latex formed such particle size

distribution and variation of monomer conversion with reaction time gives a good indication of the stability of the polymer latex and the rate of polymerization respectively.

As a preliminary experiment, the effect of the amount of initiator on the polymerization of vinyl acetate was tested in two runs ME-VAc 06 and ME-VAc 11. The I/M ratio in ME-VAc 11 was about (1.0% mol KPS/mol VAc), more than that in ME-VAc 06 (0.5% mol KPS/mol VAc). The conversion-time graph plot obtained through gravimetric methods is shown in Figure 4.1. Although the final monomer conversion achieved in both the runs are similar at about 92%, the rate at which this conversion is achieved is much different. ME-VAc 11 achieves this value in about 40 minutes while it takes about 120 minutes for ME-VAc 06 to achieve this monomer conversion. This is because of the fact that a high initiator concentration results in an increase in the amount of radicals available to initiate the polymerization, and hence a faster polymerization. The initiator to monomer ratio was not increased beyond the value in ME-VAc 11 in other subsequent experiments involving vinyl acetate homo-polymerization.

The particle size distribution of ME-VAc 11 is depicted in Figure 4.2. As it can be seen, there is a shift in the mean particle size of the distribution at 124.7 nm after polymerization, to 150.6 nm one week after polymerization, to 217.5 nm two weeks after the polymerization run. This unstable particle size distribution is caused by coagulation of particles in the latex due to insufficient stabilization by the surfactant. The next section presents how the surfactant concentration affects the stability of the latex.

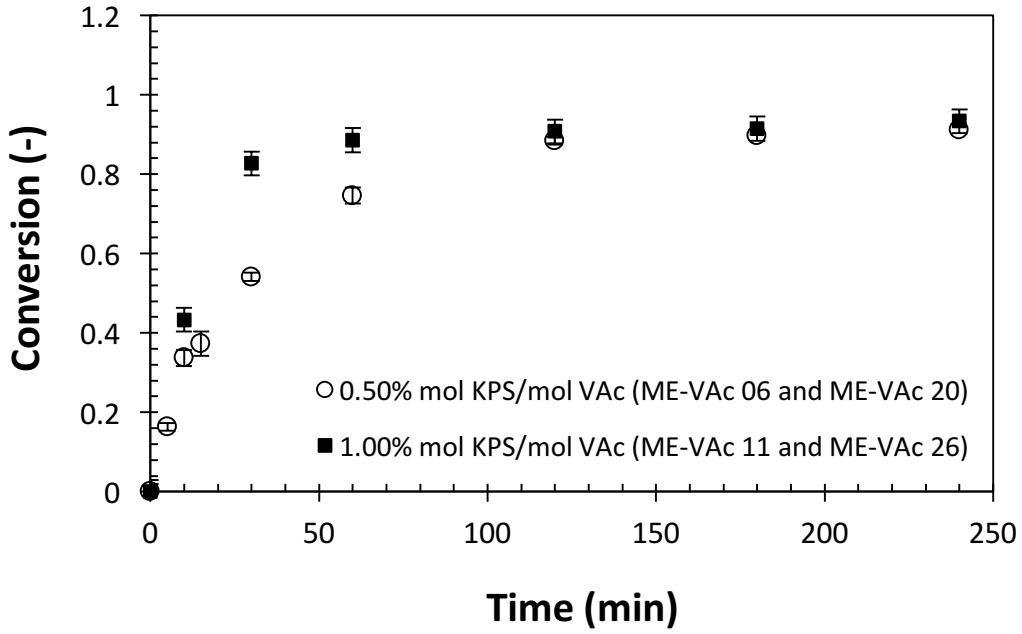


Figure 4.1. Conversion versus time plot of two runs at different initiator concentrations – 0.50% mol KPS/mol VAc (ME-VAc 06 and ME-VAc 20) and 1.00% mol KPS/mol VAc (ME-VAc 11 and ME-VAc 26), with other reaction conditions being the same.

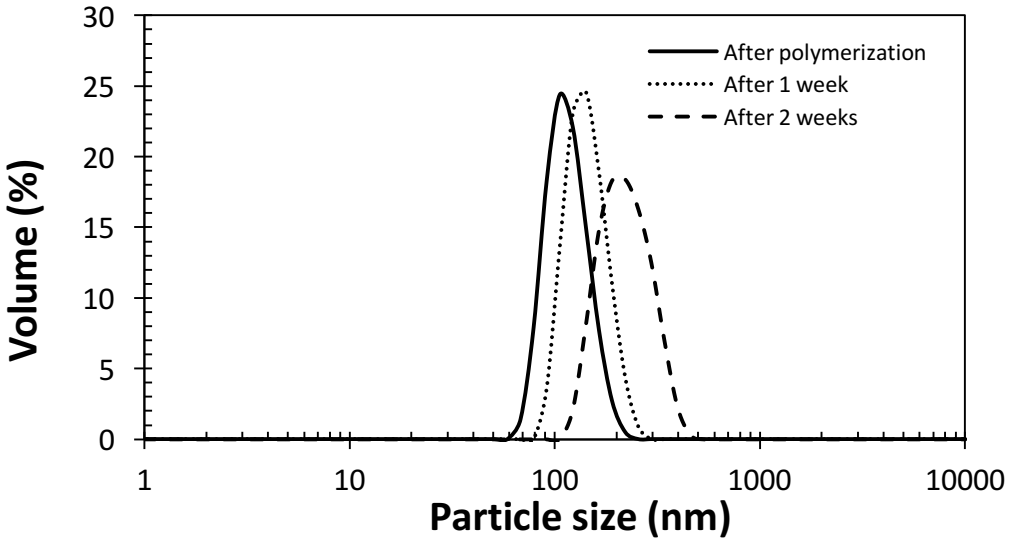


Figure 4.2. Particle size distribution of an unstable latex (ME-VAc 11) due to insufficient stabilization by surfactant.

4.2.2. Effect of surfactant

The surfactant used can have a crucial effect on the particle size & distribution, viscosity and the overall latex stability of the copolymer. Sodium dodecyl sulfate (SDS) has been used as the anionic surfactant in this study. Varying the ratio of surfactant concentration to monomer (S/M) concentration and observing the properties of the latex formed such particle size distribution gives a good indication of the stability of the polymer latex.

The effect of the amount of surfactant on the polymerization of vinyl acetate was compared between two runs ME-VAc 11 and ME-VAc 12. The S/M ratio in ME-VAc 12 was about 1.5 times as that in ME-VAc 11. The conversion time graph plot obtained through

gravimetric methods is shown in Figure 4.3. The conversion time profiles obtained in the two cases are quite similar, with ME-VAc 11 having a slightly higher conversion than ME-VAc 12. Although it may seem that changing the S/M ratio in Me-VAc 11 has not helped with improving the conversion of monomer, a look at the particle size distribution in Figure 4.4 shows better results.

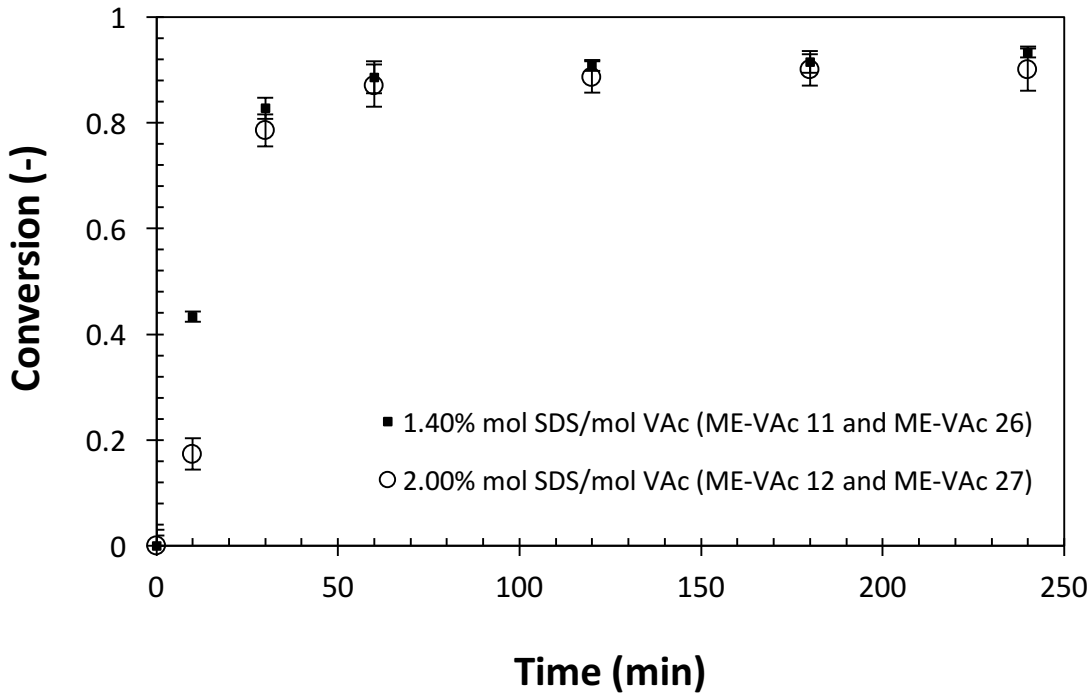


Figure 4.3. Conversion versus time plot of two runs at different surfactant concentrations – 1.40% mol SDS/mol VAc (ME-VAc 11 and ME-VAc 26) and 2.00% mol SDS/mol VAc (ME-VAc 12 and ME-VAc 27), with other reaction conditions being the same.

As it can be seen, the mean particle size of the distribution remains relatively stable at 104.4 nm after polymerization, to 109.9 nm one week after polymerization, to

115.8 nm two weeks after the polymerization run. The stability is achieved as a result of increased emulsification of reactive monomers and the formation of stable dispersion of polymer particles in ME-VAc 12. The surfactant to monomer ratio was not changed beyond the value in ME-VAc 12 in other subsequent experiments involving vinyl acetate homo-polymerization.

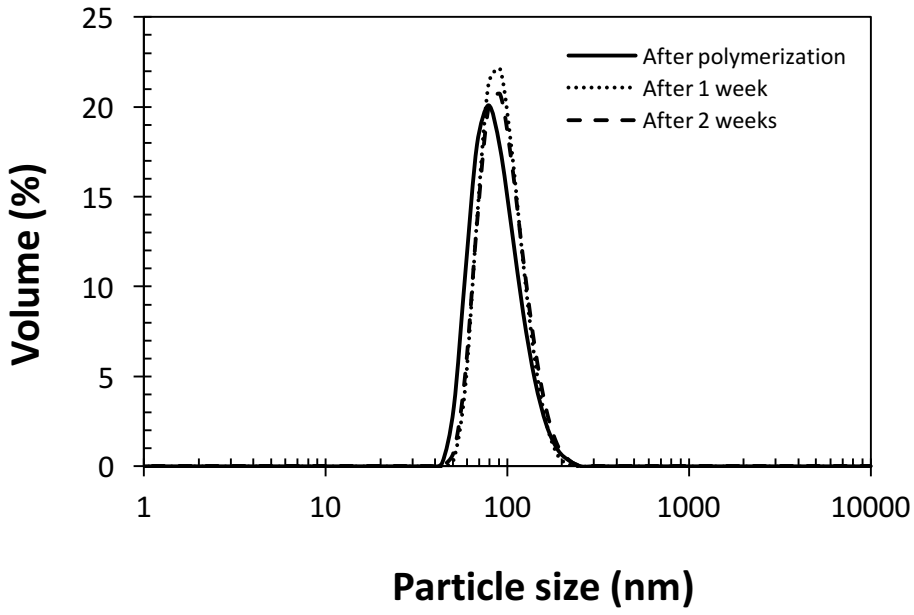


Figure 4.4. Particle size distribution of a stable latex (ME-VAc 12), due to sufficient stability provided by surfactant (2.00% mol-SDS/mol-VAc).

4.2.3. Effect of Monomer Concentration

A good surfactant/monomer (S/M) ratio ensured the stability of the polymer latex formed. The monomer concentration was now increased keeping a constant S/M ratio.

The TSC and conversion versus time plots are shown in Figures 4.5 and 4.6 respectively. Although the final monomer conversion of monomer remains the same at around 86%, it can be seen that the total solids content has increased from around 14% in ME-VAc 01 to around 22% in ME-VAc 03.

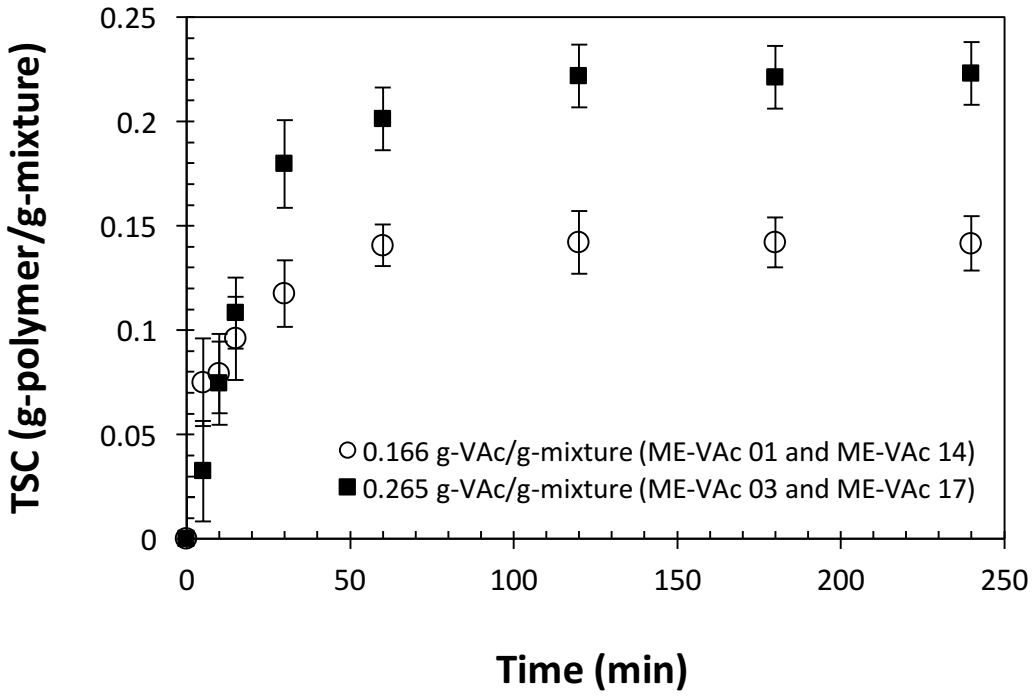


Figure 4.5. Total solids content (g-polymer/g-mixture) versus time (min) profile for VAc homo-polymerization experiments with different monomer concentrations – 0.166 g-VAc/g-mixture (ME-VAc 01 and ME-VAc 14) and 0.265 g-VAc/g-mixture (ME-VAc 03 and ME-VAc 17), with other reaction conditions being the same.

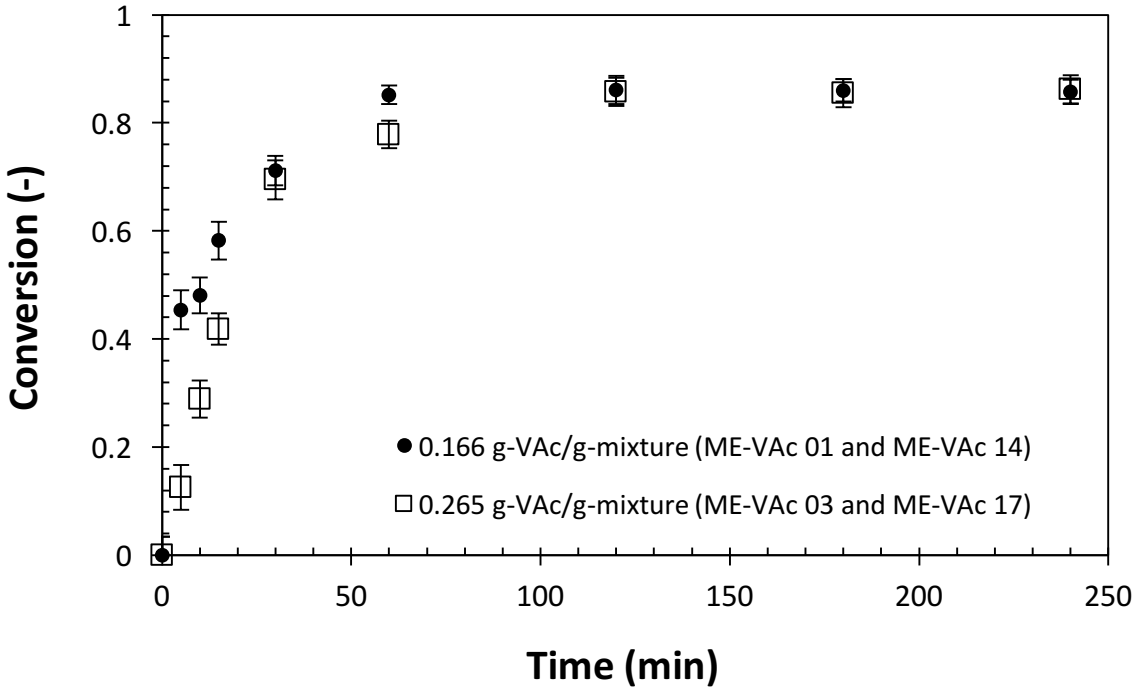


Figure 4.6. Conversion (-) versus time (min) profile for VAc homo-polymerization experiments with different monomer concentrations – 0.166 g-VAc/g-mixture (ME-VAc 01 and ME-VAc 14) and 0.265 g-VAc/g-mixture (ME-VAc 03 and ME-VAc 17), with other reaction conditions being the same.

4.3. Vinyl Acetate Miniemulsion Homo-polymerization

The next set of the preliminary studies involved conducting some baseline experiments for miniemulsion polymerization. Miniemulsion polymerization was done by homogenizing for this run. The TSC of a miniemulsion polymerization was initially compared with an emulsion polymer keeping all the reaction conditions the same, as shown in Figure 4.7. The total solid content reaches a value of about 14% in the normal

emulsion while it reaches about 15% in miniemulsion. The two curves are almost identical goes in to show the excellent agitation in place combined with the better solubility of VAc in water, that reduce the mass transfer limitations in both emulsion and miniemulsion VAc homo-polymerization. The case is however different when ethylene is added into the mixture as a comonomer in VAE copolymerization, which are described in more detail in Chapters 5 and 6. It can also be noted that rates of polymerization in both cases are almost the same which can be attributed to similar I/M ratios in both cases. Figures 4.8 shows the conversion time profile of the both runs. The conversion reaches a value of about 85% in normal emulsion run and about 90% in the miniemulsion run. The reason why the conversion did not reach higher values was probably because of gel effect, a phenomenon caused by decrease in termination rate constants at higher conversions because of lower mobility of polymer chains [36]. Since it is a homo-polymerization run, there is direct conversion between the TSC and the correspond monomer conversion at that point. The calculation becomes a little more complicated in a copolymerization where the total solids content comprises of both monomers and the composition of the copolymers needs to be measured before calculating the conversion.

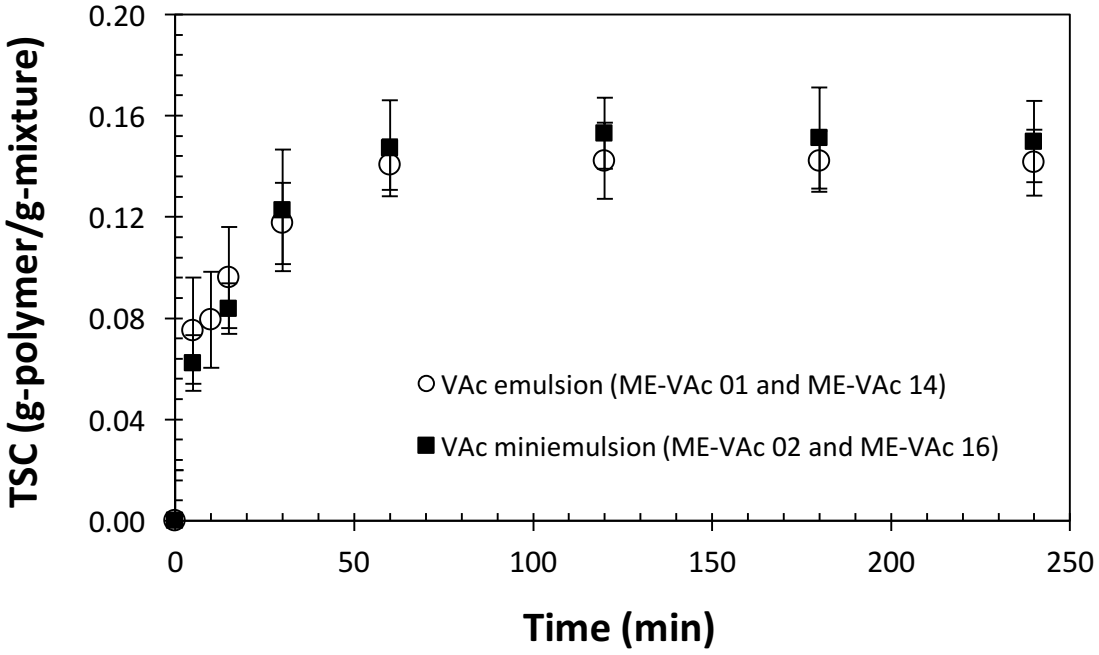


Figure 4.7. Total solids content (g-polymer/g-mixture) versus time (min) profile of VAc emulsion (ME-VAc 01 and ME-VAc 14) and miniemulsion by homogenizing (ME-VAc 02 and ME-VAc 16) homo-polymerization made under similar reaction conditions.

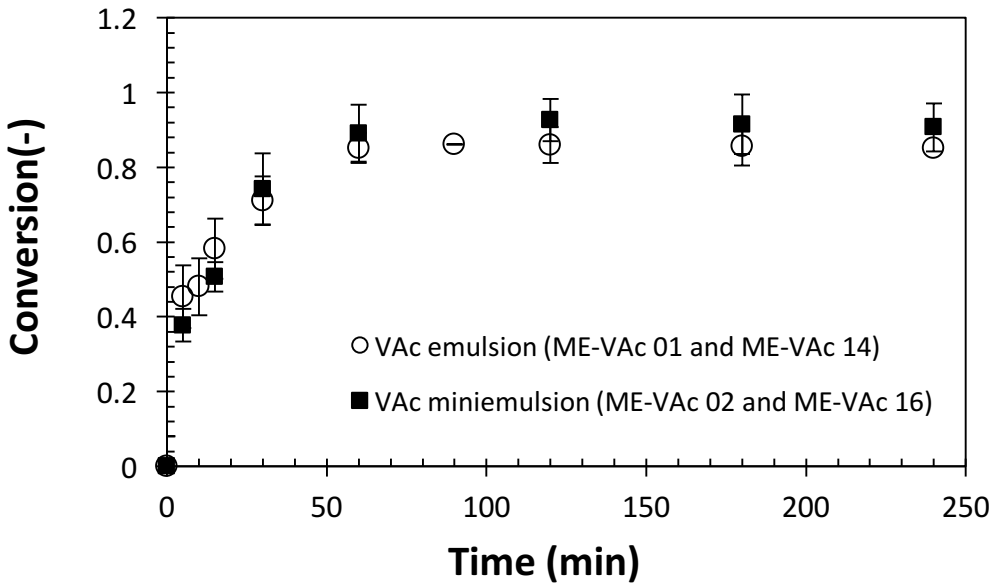


Figure 4.8. Conversion (-) versus time (min) plot of VAc emulsion (ME-VAc 01 and ME-VAc 14) and miniemulsion by homogenizing (ME-VAc 02 and ME-VAc 16) homo-polymerization made under similar reaction conditions.

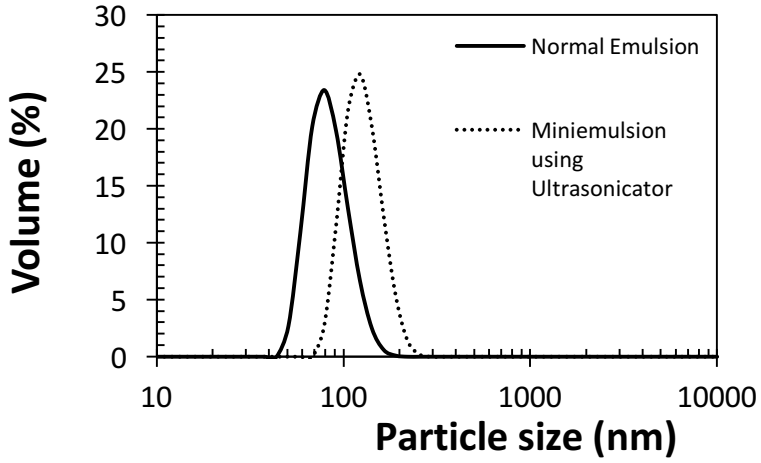


Figure 4.9. Particle size distribution of emulsion and miniemulsion (by ultrasonication) VAc homo-polymerization made under similar reaction conditions.

Ultrasonication is the other method employed in order to obtain a miniemulsion. Figure 4.9 shows a plot of the total solids content (TSC) versus time profiles of two runs ME-VAc 03 and MU-VAc 04. ME-VAc 03 is normal emulsion while MU-VAc 04 is a miniemulsion. The mean particle size of the miniemulsion is higher than of the normal emulsion. Similar results were observed by some authors [37], where when emulsions and miniemulsions were produced under identical conditions, the particle sizes of miniemulsions were greater than that observed in emulsions.

Miniemulsions are made by the application of high shear force on a normal emulsion. In order to study the differences in particle stability of miniemulsion latex obtained by both homogenizing and ultrasonication, the particle size distributions of two runs MH-VAc 02 and MU-VAc 04 are shown in Figure 4.10. Although both the methods produce distributions that remain stable even two weeks after polymerization, it can be noted that ultrasonication produces a narrower distribution in particle sizes [37]. Generating a minemulsion from an emulsion was primarily done by ultrasonication in the study. Although miniemulsion obtained via ultrasonication had narrow particle size distributions, they are much costlier to perform as compared to using a homogenizer and are not feasible at an industrial scale.

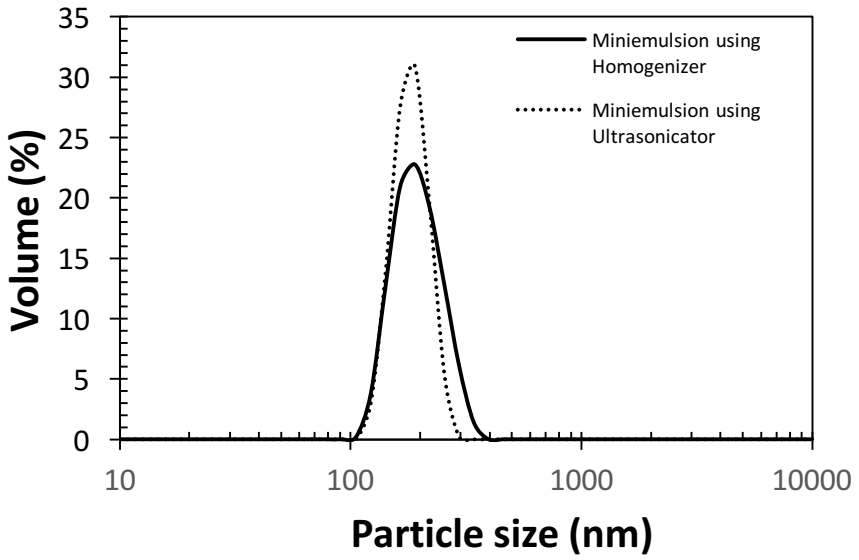


Figure 4.10. Particle size distribution of two VAc miniemulsion homo-polymerization runs generated by different methods, other reaction conditions being the same.

4.4. Conclusions

Emulsion and miniemulsion homo-polymerization of vinyl acetate has been conducted at different experimental conditions. Increasing the initiator concentration improved the rate of polymerization while increasing the surfactant concentration improved the stability of particle sizes observed over time. Increasing the agitation in high pressure reactors reduced the gel effect thereby improving the monomer conversion. The particle size distribution of a VAc polymer latex produced by ultrasonication was narrower than that produced by homogenization, and the particle sizes were slightly higher than that produced by conventional emulsion.

CHAPTER 5

EMULSION COPOLYMERIZATION OF VINYL ACETATE AND ETHYLENE

5.1. Introduction

This chapter presents experimental results, analysis and discussion of low and high pressure emulsion copolymerization of vinyl acetate and ethylene (VAE). The reaction conditions for the experiments involving emulsion copolymerization of vinyl acetate with ethylene are shown in Appendix A.2. The experimental runs have been sorted in the Table in the order of increasing ethylene pressure. All the polymerization runs have been either conducted in the low pressure glass reactor or the high pressure autoclave reactor, and have been indicated so in the table. The total volume of constituents in the low pressure was almost just half as much as the volume of contents in the high pressure reactor. To ensure good mixing, the agitation speed was set to 400 rpm in the low pressure glass reactor and to 700 rpm in the high pressure autoclave reactor taking the volume of contents into consideration.

Figure 5.1 shows a plot of total solids content (g-polymer/g-mixture) against time (min) for VAE emulsion copolymerization run as compared to a VAc emulsion homo-polymerization run made with similar VAc monomer concentration. The initiator concentration was kept at the same level as that in vinyl acetate emulsion homo-

polymerization experiments. The TSC reached a value of about 25% towards the end of the VAE run, which is slightly lesser than what would be observed had all the VAc in the mixture polymerized, but considerably more than that of the VAc homo-polymerization run, whose TSC at the end of the run is only about 22%. Neglecting the weight of SDS and KPS in the mixture, this difference in TSC is mainly because of ethylene incorporation in VAE emulsion copolymer. Unlike the vinyl acetate homo-polymerization experiments where the monomer conversion could easily be derived from the total solids content, the TSC in VAE copolymerization describes the total solid polymer content which comprises of both vinyl acetate and ethylene.

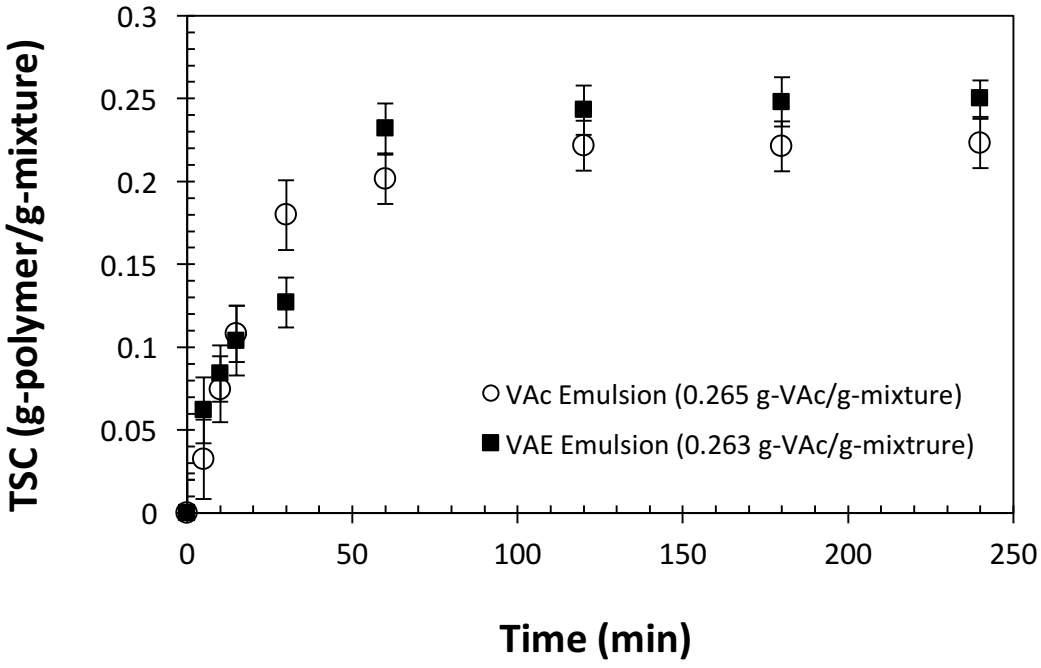


Figure 5.1. Total solids content (g-polymer/g-monomer) versus time (min) profile for VAE emulsion copolymerization (0.263 g-VAc/g-mixture; ME-VAE 04 and ME-VAE 49) and VAc emulsion homo-polymerization (0.265 g-VAc/g-mixture; ME-VAc 03 and ME-VAc 17).

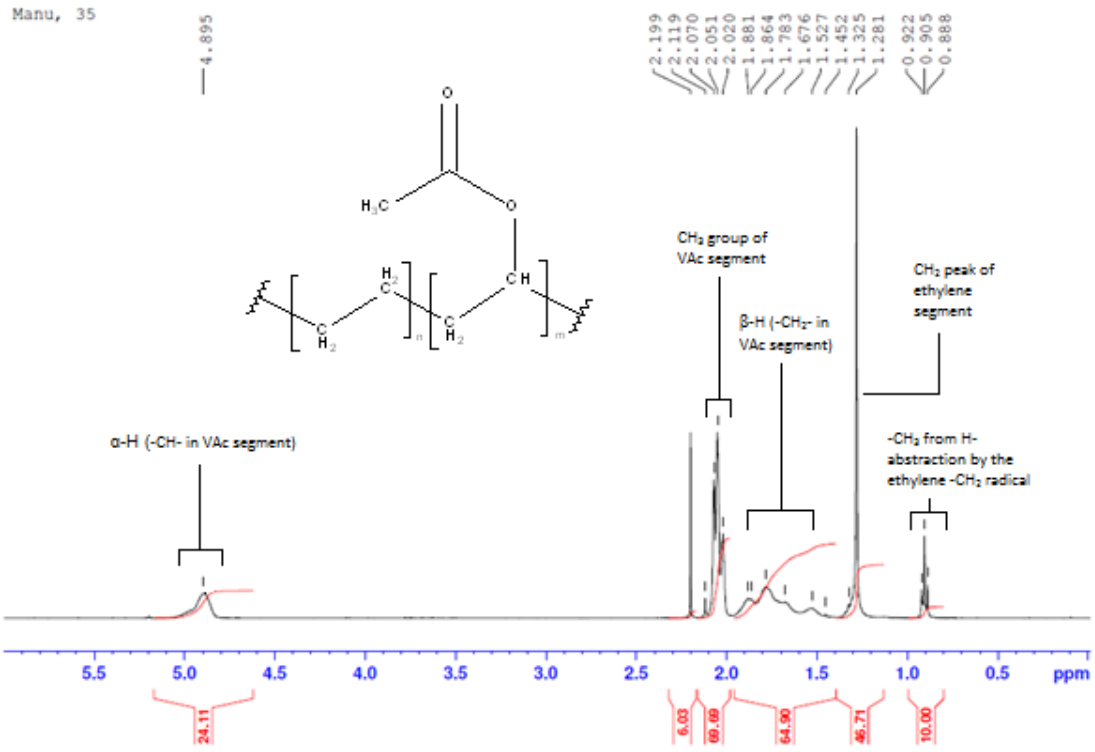


Figure 5.2. ^{1}H NMR spectrum of a VAE emulsion copolymer.

In order to find the composition of the copolymer, ^{1}H NMR tests are done to the dried copolymer samples. Figure 5.2 shows a sample ^{1}H NMR spectrum whose data will be used to determine the VAc conversion. As described in Equation 3.2, the molar ratio of ethylene to vinyl acetate in the copolymer is equal to 0.796 (mol-Eth/mol-VAc). The method used to derive the conversion of vinyl acetate monomer from the TSC and ^{1}H NMR data is described in the calculations below.

Sample Calculation: Obtaining VAc conversion from TSC and ^{1}H NMR data

Moles of ethylene per mole of vinyl acetate from ^{1}H NMR data = 0.796 (mol-Eth/mol-VAc)

$$\text{Mass of ethylene(g) per gram of vinyl acetate } = \frac{0.796 \times 28.05}{1 \times 86.09} = 0.259 \text{ (g-Eth/g-VAc)}$$

$$\text{Ethylene mass fraction in copolymer} = \frac{0.259}{1 + 0.259} = 0.206$$

$$\text{Vinyl acetate mass fraction in copolymer } = 1 - 0.206 = 0.794$$

Assuming the wet weight and dry weight of the collected sample (at t = 240 min) is 0.756 g and 0.189 g respectively.

From Appendix A.2, neglecting the mass of KPS and SDS,
mass of vinyl acetate per gram of the reaction mixture is $= \frac{(0.456 \times 86.02)}{(6.11 \times 18)+(0.456 \times 86.02)} =$ 0.263

If all the vinyl acetate had polymerized, mass of vinyl acetate in copolymer would be = 0.263 x 0.756 = 0.199 g.

However,

$$\text{actual mass of vinyl acetate in collected sample} = 0.794 \times 0.189 = 0.150 \text{ g}$$

$$\text{Hence, conversion of vinyl acetate } = \frac{0.150}{0.199} = 0.75 \text{ or } 75\%$$

5.2. Varying the Total Solid Content

Gravimetric methods were employed in determining the total solids content (TSC) of a copolymer as described in the Materials and Methods section. Figure 5.3 shows the plot of TSC versus time for four experiments with different vinyl acetate monomer concentrations resulting in copolymers with varying solids content. Since all the four runs

had the same surfactant concentration, the surfactant to monomer ratio was different in each run. A study of the particle size distribution of the copolymer latex after the run gave a good idea about the stability of the latex formed. Figures 5.4 depicts the particle size distributions of the four runs. As the concentration of monomer is increased, the total solid content also increases from about 25% in ME-VAE 04 to around 35% in ME-VAE 07.

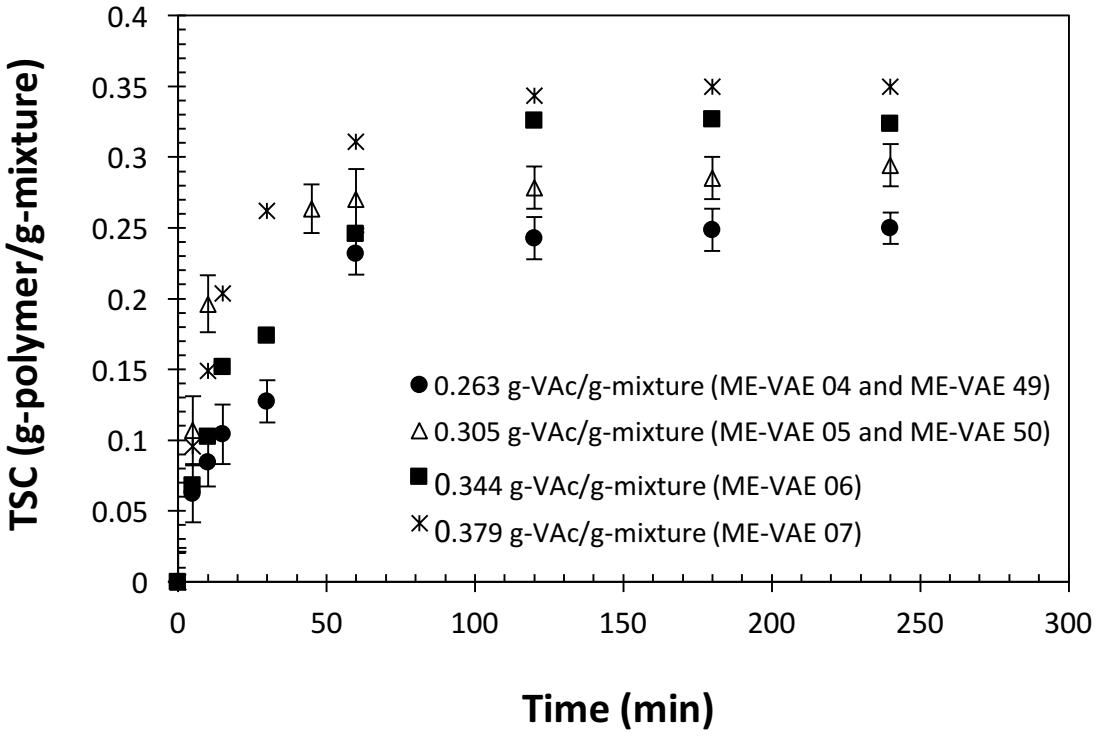
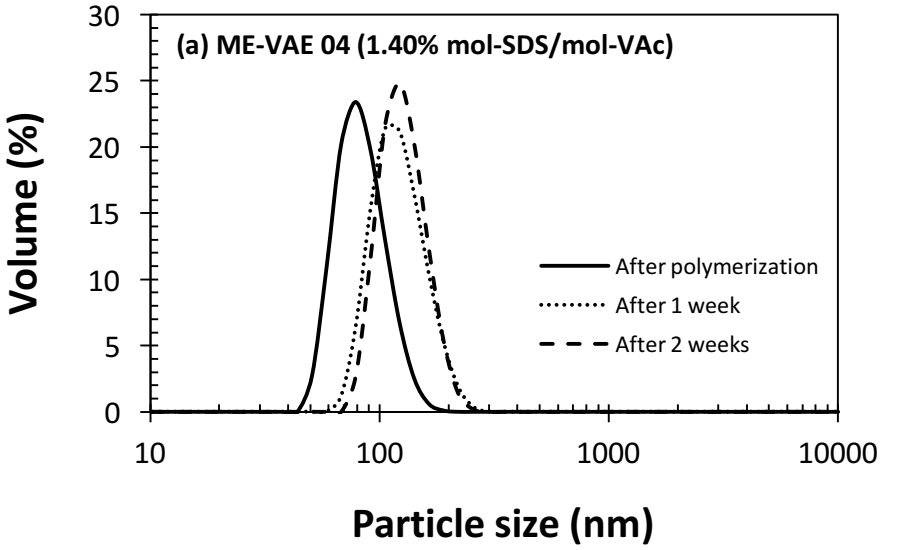
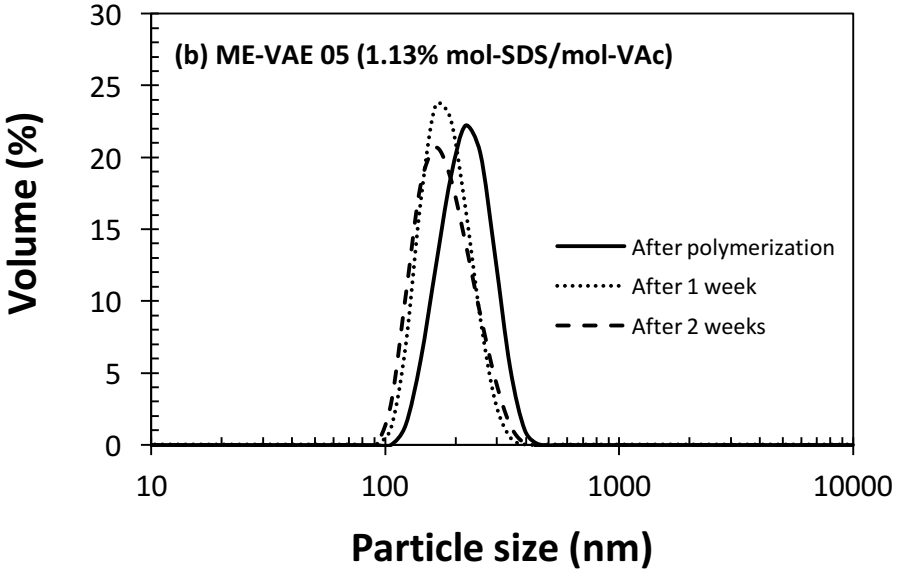


Figure 5.3. Plot of total solids content (g-polymer/g-mixture) versus time (min) for four experiments with different monomer concentrations, other reaction conditions being similar.

For the given surfactant amount, ME-VAE 05 seemed to be the most stable with respect to particle sizes measured over a time period of two weeks. As can be seen, ME-VAE 05 appears to be more stable than the others over the 2 week period following polymerization run.





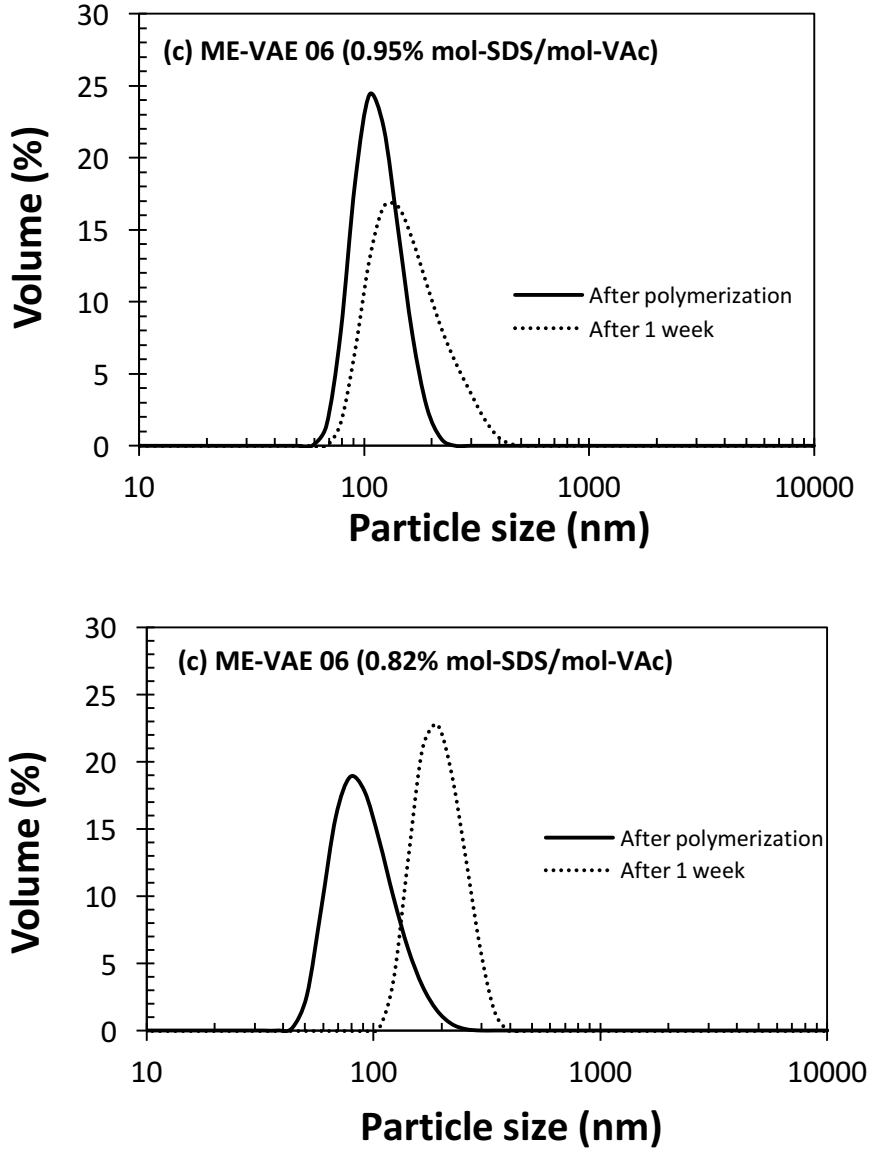


Figure 5.4. Particle size distributions of VAE copolymers with different surfactant/monomer ratios: (a) ME-VAE 04 (1.40% mol-SDS/mol-VAc), (b) ME-VAE 05 (1.13% mol-SDS/mol-VAc), (c) ME-VAE 06 (0.95% mol-SDS/mol-VAc) and (d) ME-VAE 07 (0.82% mol-SDS/mol-VAc).

ME-VAE 06 and ME-VAE 07 coagulated and solidified after a period of 2 weeks, and hence their particle sizes could not be measured after the first week. The reason for coagulation was possibly because of insufficient stabilization provided by the surfactant. Hence there was a need to find the right surfactant to monomer ratio that would ensure polymers latexes that would stable at least for a period of 4-5 weeks. Surfactants have a crucial effect on the conversion, particle size, distribution, viscosity, overall latex stability and the cleanness of the copolymer. In addition, surfactants also affect the final properties such as film formation, adhesion, wettability, water resistance and foamability. Lower SDS concentrations result in incomplete conversion of monomer vinyl acetate to polymer phase, while very high SDS concentrations have resulted in particle coagulation and subsequent fouling of polymer latex. Figure 5.5 describes the mean particle size (nm) as a function of time (days) of four VAE emulsion copolymerization runs with different S/M molar ratios. ME-VAE 05 (S/M = 1.13% mol-SDS/mol-VAc) was the most stable sample with the longest durability before coagulation after 5 weeks.

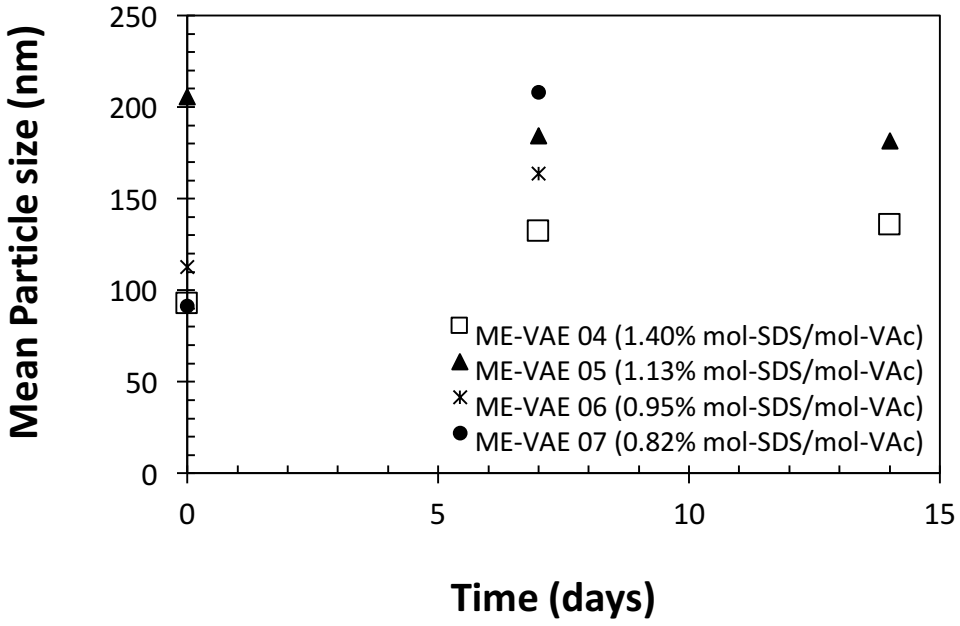


Figure 5.5. Mean particle size (nm) as a function of time (days) of four VAE emulsion copolymerization runs with different S/M molar ratios: ME-VAE 04 (1.40% mol-SDS/mol-VAc), ME-VAE 05 (1.13% mol-SDS/mol-VAc), ME-VAE 06 (0.95% mol-SDS/mol-VAc) and ME-VAE 07 (0.82% mol-SDS/mol-VAc).

In order to determine and further confirm the right amount of surfactant concentration that will give a coagulation-free latex without compromising on the monomer conversion, a number of experiments with varying surfactant concentrations were carried out. Figure 5.6 shows the particle size distribution of a stable emulsion made in the high pressure reactor (ME-VAE 45) whose distribution continued to remain stable over a period of 2 weeks. The surfactant/monomer mole ratio was 1.00% (mol-SDS/mol-VAc).

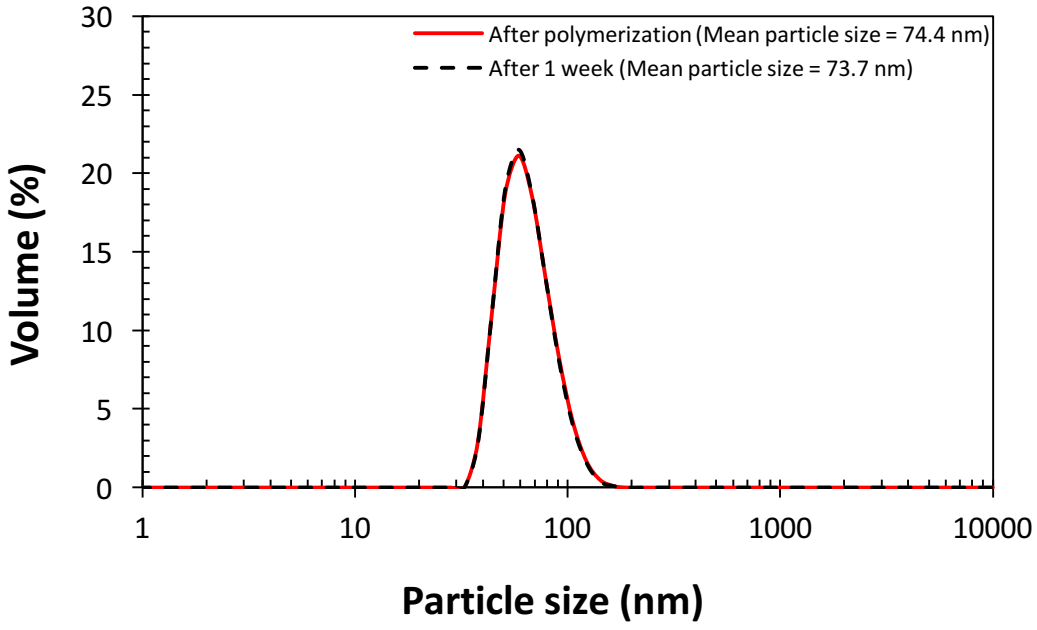


Figure 5.6. Particle size distribution of a very stable emulsion (ME-VAE 45), with a surfactant concentration of 1.00% mol-SDS/mol VAc.

5.3. Monomer conversion at different time points

As shown before in Figure 5.3, the TSC describes the total solid polymer content which comprises of both vinyl acetate and ethylene. An interesting aspect would be to study the manner in which ethylene gets incorporated into the copolymer at different time points for a conventional emulsion and later in a miniemulsion in the following chapter. Appendix A.1 shows the ^{1}H NMR spectra of samples taken at different time points for the run ME-VAE 45. Table 5.1 summarizes the calculation made based on the NMR data. It determines the amount of ethylene that has been incorporated into the copolymer at different time points during a reaction for a normal emulsion.

Table 5.1. Summary of ^{1}H NMR spectra of samples taken at different time points for conventional VAE emulsion copolymerization ME-VAE 45 (0.159 g-VAc/g-mixture, 80 psig Eth, 0.97% mol-SDS/mol-VAc, 0.31% mol-KPS/mol-VAc, 60°C, 400 rpm)

Time (min)	Sample wet weight (g)	VAc weight in sample (g)	Et/VAc (mol/nol)	Et mol fraction (mol/mol)	VAc mol fraction (mol/mol)	Et wt. fraction (g/g)	VAc wt. fraction (g/g)	Sample dry weight (g)	VAc conversion (-)
15	1.545	0.237	0.178	0.151	0.849	0.055	0.945	0.082	0.326
20	3.076	0.471	0.173	0.147	0.853	0.053	0.947	0.240	0.483
30	2.453	0.376	0.154	0.133	0.867	0.048	0.952	0.343	0.870
120	1.134	0.174	0.195	0.163	0.837	0.060	0.940	0.162	0.875
180	1.029	0.158	0.234	0.190	0.810	0.071	0.929	0.147	0.865
240	1.807	0.277	0.244	0.196	0.804	0.074	0.926	0.259	0.868

Figure 5.7 represents the VAc conversion data in Table 5.1. It shows both the VAc conversion and TSC data on the primary and secondary axis of the same plot respectively. The TSC reaches about 14.3% at the end of this run while the vinyl acetate monomer conversion reaches a value of about 87% at the end of the run. There is a very good correlation between the conversion and TSC data, and this is a good indicative of random copolymerization with reactivity ratios of vinyl acetate and ethylene being close to unity [2]. Had the vinyl acetate conversion showed a slower increase as compared to TSC, it would indicate a higher preference towards ethylene addition during copolymerization in those parts of the graph. This is because the increase in the total solids content of the copolymer represents a contribution from both vinyl acetate as well as ethylene. It also follows that a slower increase of TSC in comparison to the vinyl acetate conversion implies

that the vinyl acetate is getting polymerized faster and getting incorporated into the copolymer at a faster rate relative to ethylene.

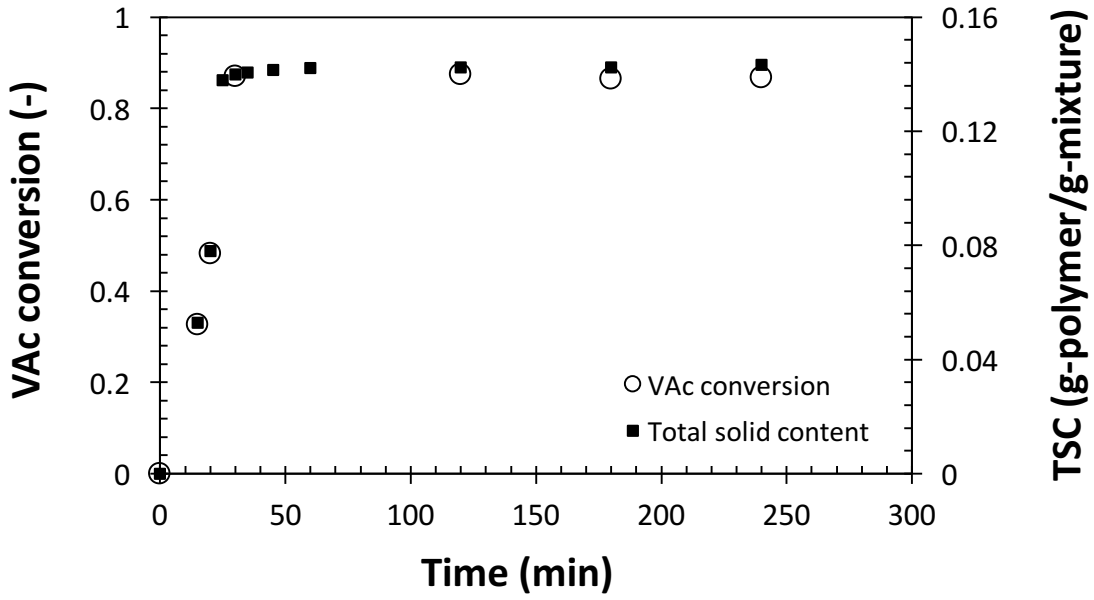


Figure 5.7. Monomer conversion (-) and TSC (g-polymer/g-mixture) at different time points for VAE emulsion copolymerization.

5.4. Particle size distribution at different time points

Similar to measuring the composition of copolymer latex at different time points during the run, the particle sizes were also measured at different time points to observe the differences between how the particle sizes changed during the run in a normal emulsion as well as a miniemulsion. The particle size distribution at different time points for a miniemulsion is shown in the next chapter. Figure 5.8 describes this PSD for a normal

emulsion run ME-VAE 43. It can be seen that during the earler stages of the polymerization, the mean particle size is as high 566.3 nm at time t = 10 min and 562.1 nm at time t = 15 min. As time progresses, the mean particle size shows a decrease to 96.7 nm at t = 120 min. The mean particle size at the end of the run stabilizes at 91.8 nm at t = 240 min. It can also be noted that the distribution is bimodal during the initial stages of the reaction which later becomes unimodal as the reaction progresses. The bimodality is due to the contribution of both the large monomer droplets and the smaller growing polymer particles. This is also results in a larger mean particle size. Towards the end of the reaction, there are no more large monomer droplets remaining and hence the distribution is unimodal comprising of just the polymer particles which are relatively smaller in size.

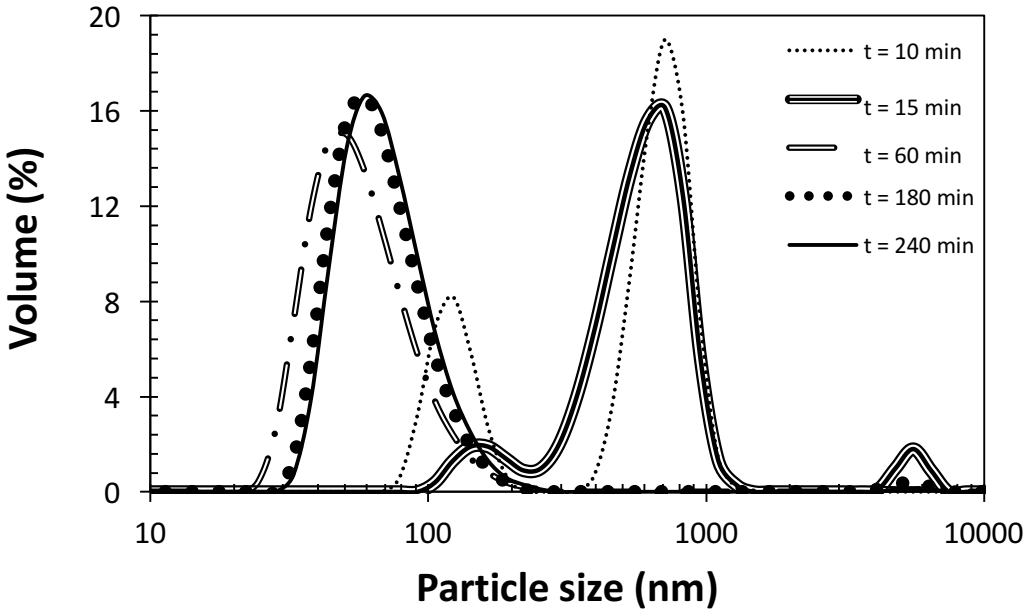


Figure 5.8. Particle size distributions of a normal emulsion run (ME-VAE 43) at different time points.

5.5. High pressure VAE emulsion copolymerization

The final part of the VAE conventional emulsion copolymerization study involves performing the copolymerization experiments at increased pressures in order to observe the manner in which ethylene gets incorporated into the copolymer and also to provide these experiments as a control for the subsequent miniemulsion copolymerization runs at increased pressures. The reaction conditions used in these high pressure experimental runs are given in Appendix A.2. ^{1}H NMR spectra of these high pressure runs are catalogued in Appendix B.1. Table 5.2 that summarizes the calculation of ethylene to vinyl acetate

ratio in the copolymer and subsequent monomer conversions from the respective ^{1}H NMR spectra.

Table 5.2. Summary of ^{1}H NMR spectra of samples taken at different pressures for VAE emulsion copolymerization

Run	Ethylene partial pressure (psig)	Et/VAc in copolymer (mol/mol)	Et mol fraction in copolymer (mol/mol)	VAc mol fraction in copolymer (mol/mol)	Et wt. fraction in copolymer (g/g)	VAc wt. fraction in copolymer (g/g)
MU-VAE 35	100	0.281	0.219	0.781	0.084	0.916
MU-VAE 51	150	0.480	0.324	0.676	0.135	0.865
MU-VAE 37	200	0.575	0.365	0.635	0.158	0.842
MU-VAE 53	250	0.843	0.457	0.543	0.215	0.785
MU-VAE 39	300	0.956	0.489	0.511	0.237	0.763

All measurements taken at the end of reaction at t = 240 min

Figure 5.9 comprehensively summarizes the Et/VAc ratios in all the normal emulsion runs at different pressures. It can be seen that as the pressure increases, the amount of ethylene getting incorporated into the copolymer shows an increase. A better description and discussion of the figure is provided at the end of Chapter 6 after the high pressure runs miniemulsion copolymerization runs.

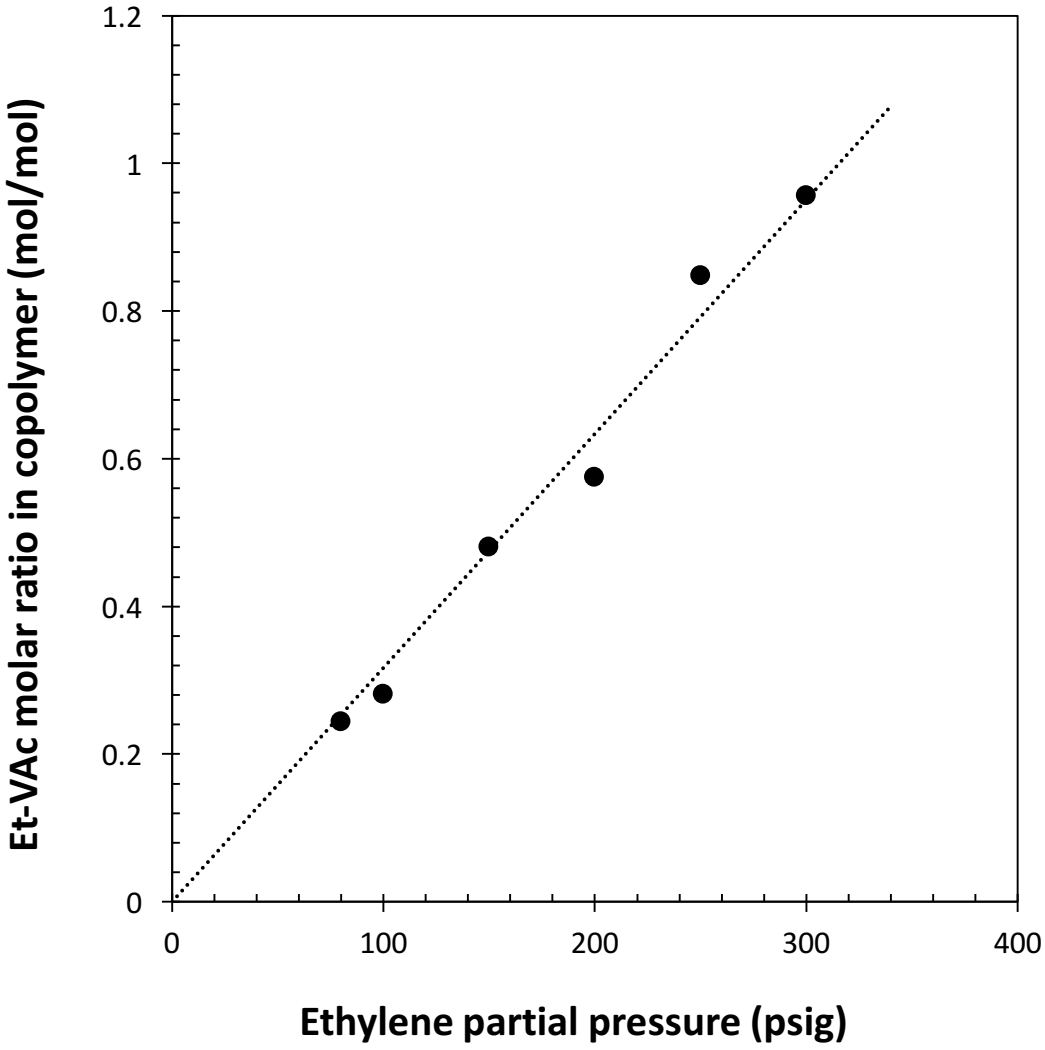
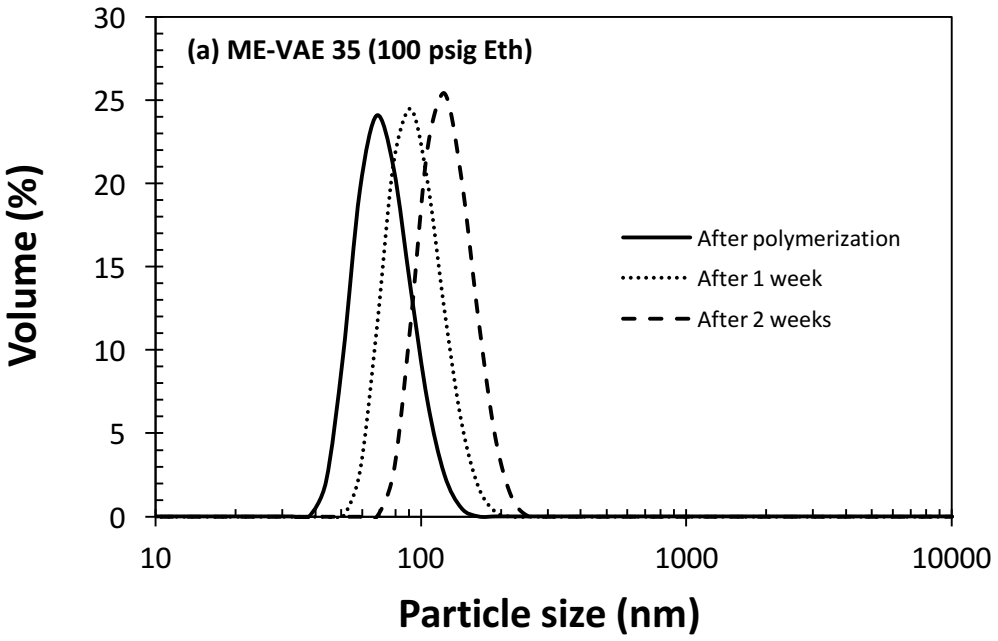
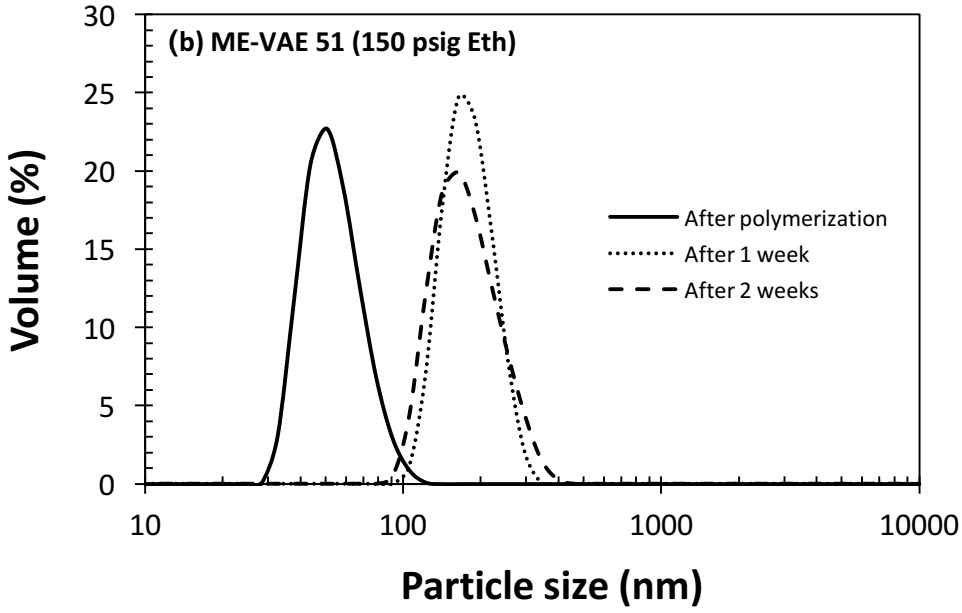


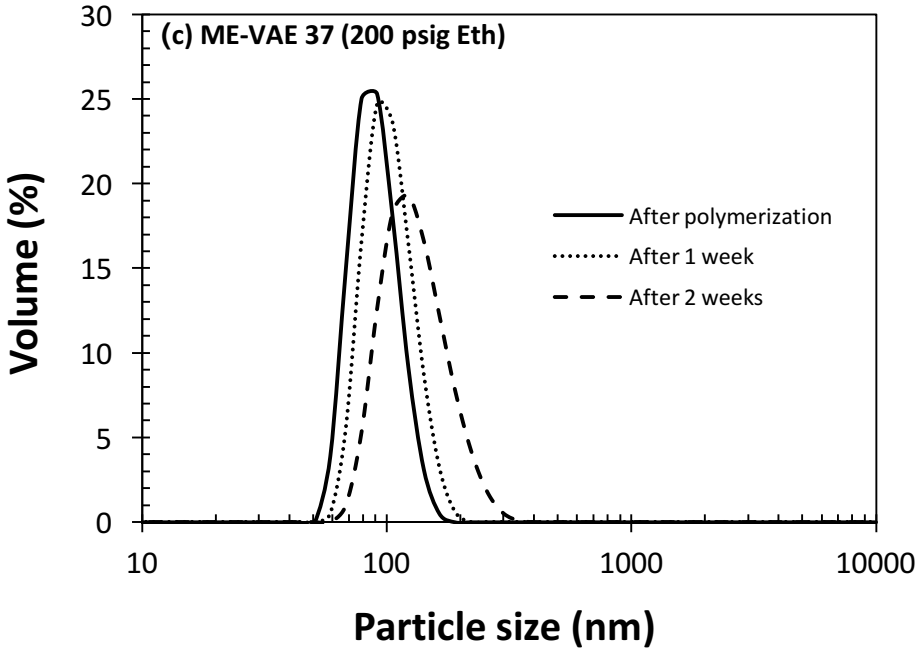
Figure 5.9. Plot of ethylene to vinyl acetate molar ratio in copolymer as a function of ethylene partial pressure (psig) for VAE emulsion copolymerization.

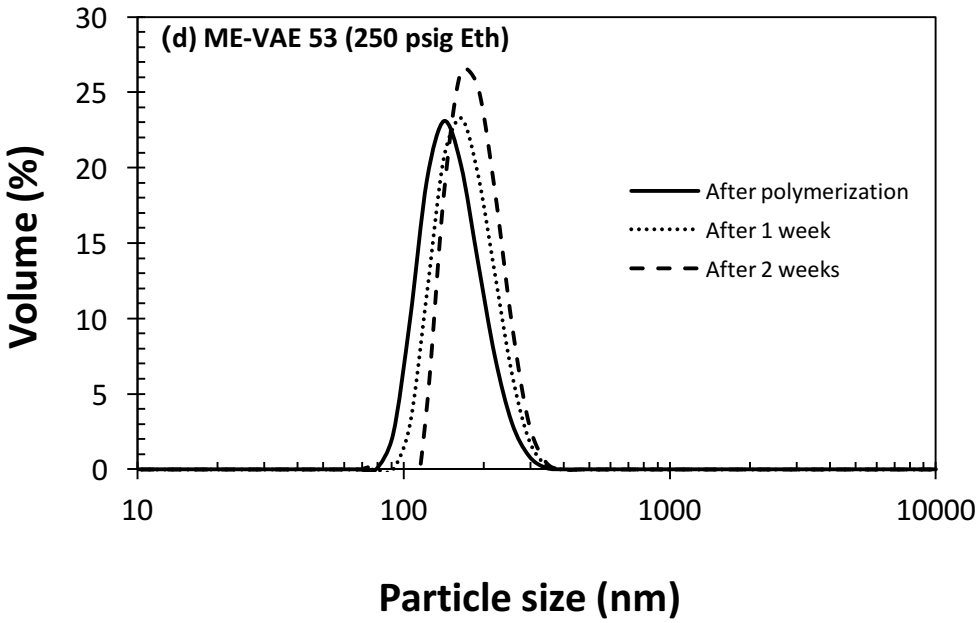
Figure 5.10 shows the particle size distributions of the above runs and Table 5.3 summarizes the mean particle sizes at different time points for these particle size distributions. Figure 5.11 summarizes Table 5.3 as it depicts a plot of how the mean

particle size changes with time. Overall, it can be seen that although the distributions obtained are narrow, they do not tend to be stable over a time period of two weeks.






(c) ME-VAE 37 (200 psig Eth)
Volume (%)
Particle size (nm)
After polymerization
After 1 week
After 2 weeks
0
5
10
15
20
25
30
10
100
1000
10000


(d) ME-VAE 53 (250 psig Eth)
Volume (%)
Particle size (nm)
After polymerization
After 1 week
After 2 weeks
0
5
10
15
20
25
30
10
100
1000
10000

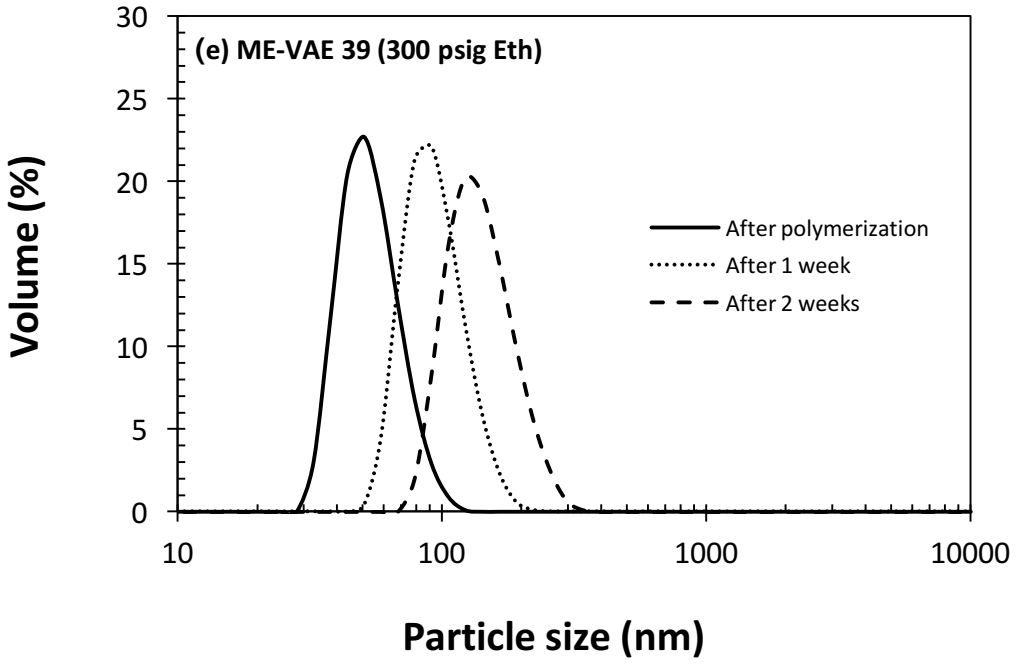


Figure 5.10. Particle size distributions of normal emulsion VAE copolymerization runs at different reaction pressures taken over a period of 2 weeks corresponding to the following runs (a) ME-VAE 35 (100 psig Eth), (b) ME-VAE 51 (150 psig Eth), (c) ME-VAE 37 (200 psig Eth), (d) ME-VAE 53 (250 psig Eth) and (e) ME-VAE 39 (300 psig Eth).

Table 5.3. Measured mean particle sizes of the distributions of emulsions prepared at different ethylene partial pressures

Run	Ethylene partial pressure (psig)	Mean particle size (nm)		
		After polymerization	After 1 week	After 2 weeks
ME-VAE 35	100	80.6	103.4	132.1
ME-VAE 51	150	82.2	188.1	194.0
ME-VAE 37	200	97.4	109.5	144.3
ME-VAE 53	250	139.2	160.4	188.3
ME-VAE 39	300	60.6	150.3	182.2

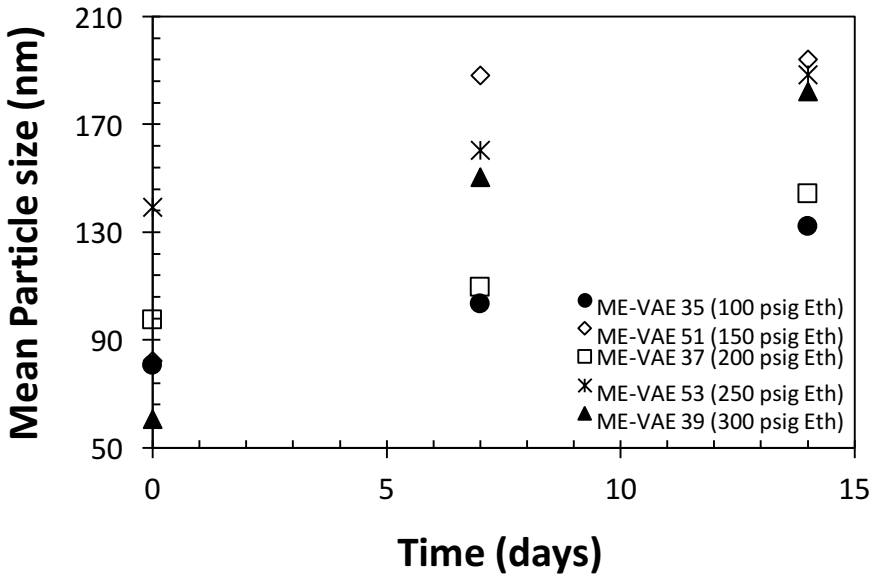


Figure 5.11. Mean particle size (nm) as a function of time (days) of four VAE emulsion copolymerization runs on the high pressure reactors at different pressures.

5.6. Viscosity Measurements

Figure 5.12 shows the dependence of viscosity with shear rate for a VAE emulsion copolymer as compared to a VAc homo-polymer. The two runs were compared such that they have similar S/M ratios and similar monomer conversions. It can be seen that the viscosity of VAE copolymer is slightly more at 2.47 x 10^{-3} Pa.s as compared to the viscosity of poly-vinyl acetate at 2.02 x 10^{-3} Pa.s. As the volume fraction of solids go up, the particles become more closely packed and it becomes more difficult for them to move around freely. Thus the particle-particle interactions increase and the resistance to flow also increases. In VAE copolymerization, ethylene that has been incorporated in the VAE

copolymer makes a difference in the overall TSC and as a result, it is reflected on the viscosity of the copolymer latex.

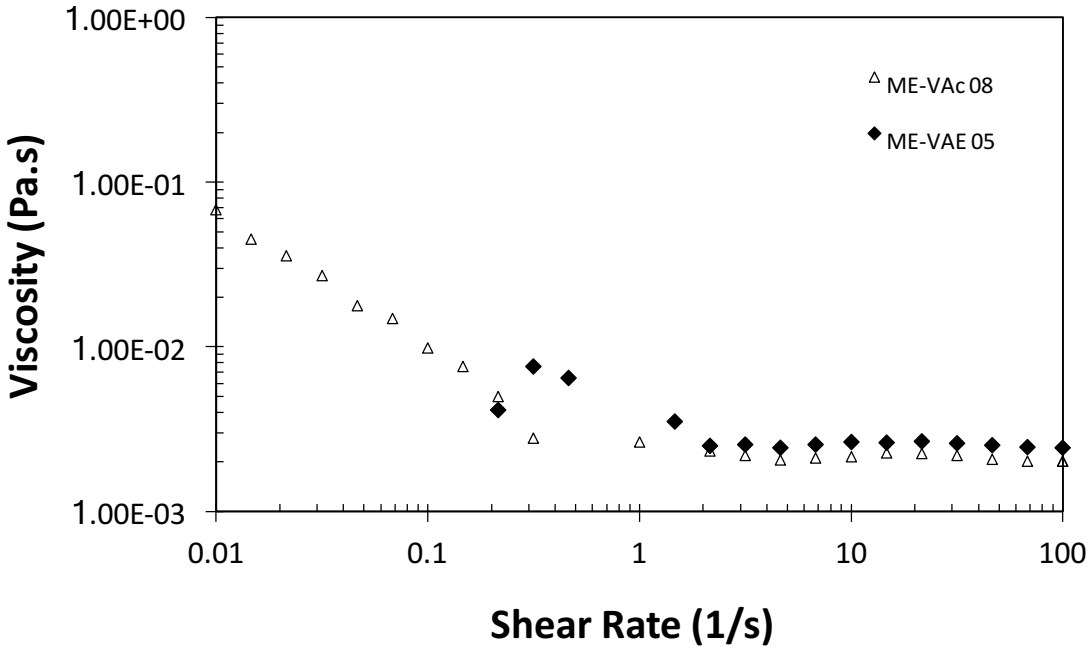


Figure 5.12. Viscosity versus shear rate for a VAE emulsion copolymer (ME-VAE 05) as compared to VAc emulsion homo-polymer (ME-VAc 08).

Figure 5.13 shows the dependence of viscosity with shear stress for two conventional emulsions, one at a lower pressure of 80 psig while the other at higher pressure of 200 psig as measured by a rheometer. The value of viscosity of the copolymer latex is taken at that when it becomes independent of shear stress. As can be seen from the figure, the viscosity of the low pressure run is 2.20×10^{-3} Pa.s, which is lower than that

of the high pressure latex whose viscosity is around 2.94×10^{-3} Pa.s. This increase in viscosity is because of the higher ethylene content that gets incorporated into the copolymer at higher pressure resulting in a higher TSC.

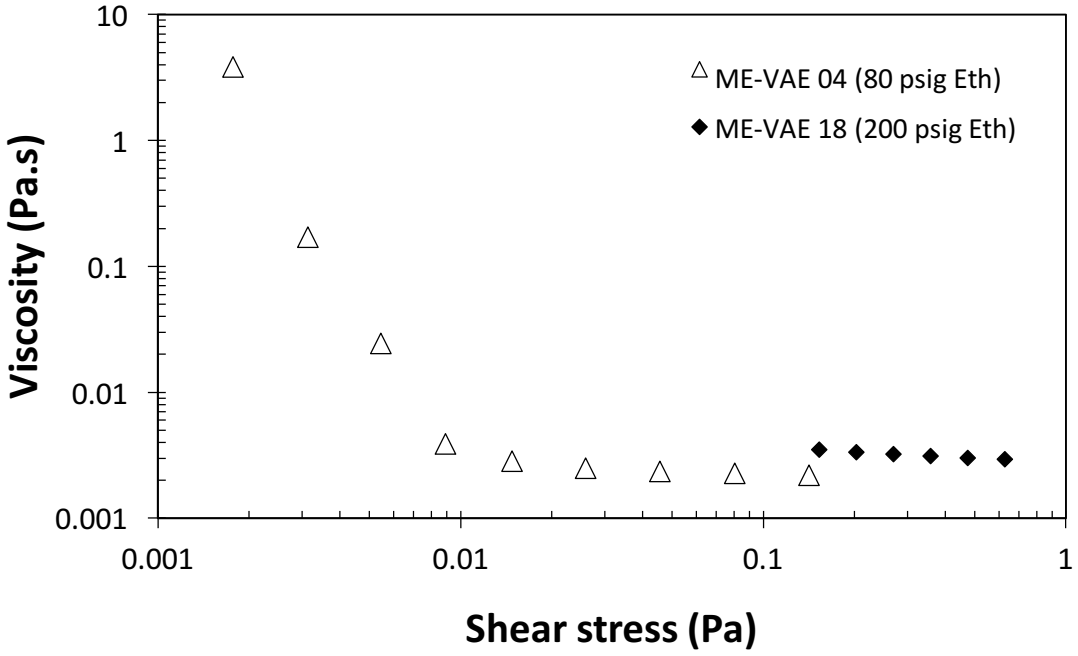


Figure 5.13. Plot of viscosity (Pa.s) versus shear stress (Pa) for two VAE emulsion copolymerization runs: one at a lower pressure of 80 psig while the other at higher pressure of 200 psig.

5.7. Conclusions

Emulsion copolymerization of vinyl acetate and ethylene has been conducted at different experimental conditions. VAE copolymers had a higher TSC (g-polymer/g-

mixture) as compared to VAc homo-polymer with similar monomer concentrations due to ethylene incorporation in the former. Increasing the monomer concentration increased the TSC of the final VAE polymer latex. An increased TSC also resulted in a higher viscosity of the final latex. Particle size distribution studies showed that the distribution was bimodal in the early stages of polymerization, due to the presence of both large monomer droplets and relatively smaller polymer particles. Increasing the ethylene partial pressure showed a corresponding increase in the ethylene/vinyl acetate molar ratio in the VAE copolymer.

CHAPTER 6

MINIEMULSION COPOLYMERIZATION OF VINYL ACETATE AND ETHYLENE

6.1. Introduction

This chapter presents experiment results, analysis and discussion of low and high pressure miniemulsion copolymerization of vinyl acetate and ethylene. The reaction conditions for the experiments involving miniemulsion copolymerization of vinyl acetate with ethylene are shown in Appendix A.3. The experimental runs have been sorted in increasing order of ethylene pressure. Just as in conventional emulsion copolymerization, all the polymerization runs have been either conducted in the low pressure glass reactor or the high pressure autoclave reactor, and have been indicated so in the table. The rates of agitation were kept the same as that in emulsion copolymerization. All experiments were conducted at 60°C.

Figure 6.1 shows the comparison of the TSC build up during the polymerization under emulsion and miniemulsion conditions for VAE copolymer, as well as the miniemulsion conditions for VAc homo-polymer. It can be seen that most of the polymerization takes place during the first one hour after which, it converges to certain value. During the first few minutes of polymerization, It can be seen that the rate of polymerization is the fastest for the VAc homo-polymer. This can be attributed to the

unperturbed polymerization of vinyl acetate without the influence of ethylene. Ethylene having a slower propagation rate constant tends to slow down the reaction as in the case of the copolymer runs. Among the copolymers, the TSC builds up faster in the emulsion as compared to that of the miniemulsion during the first one hour. This is because there is lesser ethylene dissolved in the emulsion compared to the miniemulsion, because of which there is a higher probability of the heavier vinyl acetate to polymerize as compared to ethylene. Higher presence of ethylene in the miniemulsion copolymer during the first 60 minutes has also been shown in ^{1}H proton NMR spectra that follow. As expected, for a given vinyl acetate conversion, the miniemulsion has a higher overall TSC after the 240 minute duration owing to the higher ethylene content in the copolymer as compared to the emulsion.

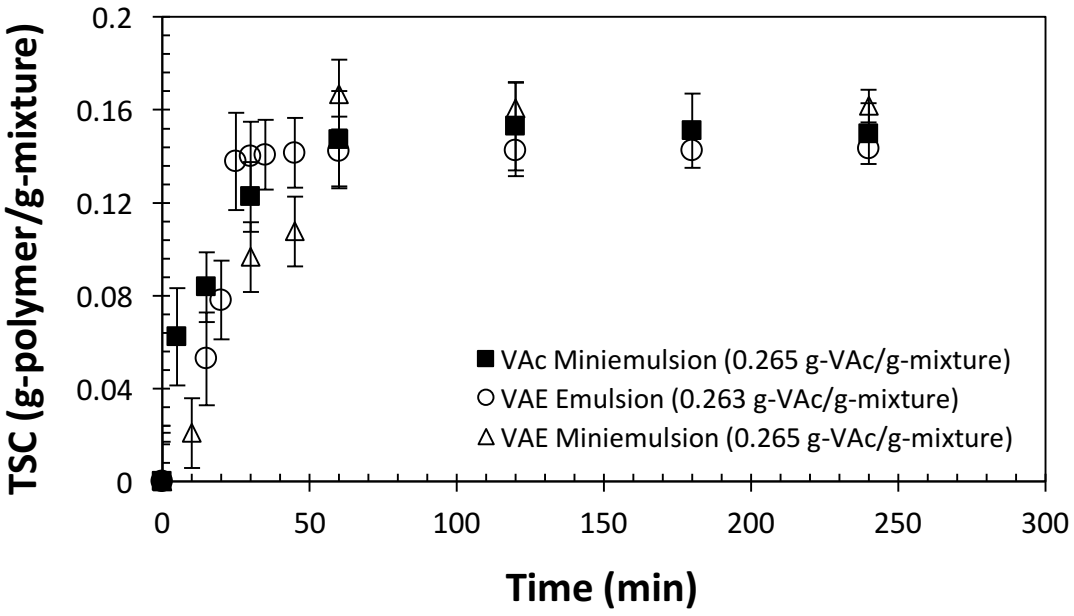


Figure 6.1. Plot of total solids content (g-polymer/g-mixture) with time (min) for VAE miniemulsion copolymer (MU-VAE 10 and MU-VAE 55: 0.265 g-VAc/g-mixture) as compared to that of VAc miniemulsion homo-polymer (MH-VAc 05 and MH-VAc 19: 0.265 g-VAc/g-mixture) and VAE emulsion copolymer (ME-VAE 04 and ME-VAE 49: 0.263 g-VAc/g-mixture).

6.2. Monomer Conversion at Different Time Points

In VAE miniemulsion copolymerization, the plot of total solids content with time describes the total solid polymer content which comprises of both vinyl acetate and ethylene. An interesting aspect would be to study the manner in which ethylene gets incorporated into the copolymer at different time points for a miniemulsion and compare the results with that obtained in a conventional emulsion in Chapter 5. The ^{1}H NMR

spectra of samples taken at different time points for the run MU-VAE 48 are given in Appendix A.2. Table 6.1 summarizes the calculation made based on this ^{1}H NMR data. It determines the amount of ethylene that has been incorporated into the copolymer at different time points during the miniemulsion run.

Table 6.1. Summary of ^{1}H NMR spectra of samples taken at different time points for VAE miniemulsion copolymerization MU-VAE 48 (0.159 g-VAc/g-mixture, 80 psig Eth, 1.16% mol-SDS/mol-VAc, 0.50% mol-KPS/mol-VAc, 7.05% mol-HD/mol-VAc, 60°C, 400 rpm)

Time (min)	Sample wet weight (g)	VAc weight in sample (g)	Et/VAc (mol/nol)	Et mol fraction (mol/mol)	VAc mol fraction (mol/mol)	Sample dry weight (g)	VAc conversion (-)
15	1.860	0.285	0.603	0.376	0.624	0.041	0.121
30	1.263	0.193	0.513	0.339	0.661	0.122	0.541
45	1.416	0.217	0.470	0.320	0.680	0.153	0.610
60	1.867	0.286	0.383	0.997	0.003	0.311	0.967
120	2.406	0.368	0.333	0.250	0.750	0.387	0.947
240	1.587	0.243	0.355	0.262	0.738	0.257	0.947

Figure 6.2 depicts the dependence of VAc conversion and overall TSC with time on the primary and secondary axis respectively. Note that both the plots develop in a similar fashion indicating the presence of random copolymerization and that the copolymer reactivity ratios are close to unity.

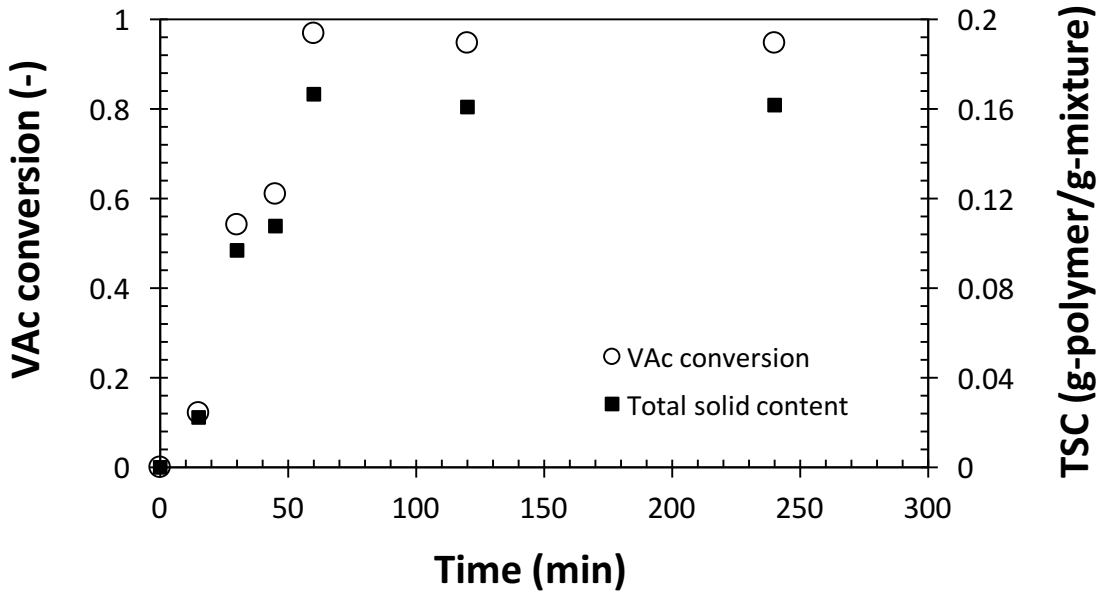


Figure 6.2. VAc conversion (-) and overall total solids content (g-polymer/g-mixture) with time (min) for VAE miniemulsion copolymerization run (MU-VAE 48: 0.159 g-VAc/g-mixture, 80 psig Eth, 1.16% mol-SDS/mol-VAc, 0.50% mol-KPS/mol-VAc, 7.05% mol-HD/mol-VAc, 60°C, 400 rpm).

Now that the vinyl acetate/ethylene molar ratio in the copolymer has been determined, the conversion of vinyl acetate into the copolymer at different time points of the reaction can be determined by simple calculations. This molar ratio of ethylene to vinyl acetate in the copolymer can help us calculate the weight of vinyl acetate present in the known weight of the extracted sample. From this, vinyl acetate conversion can be obtained since the amount of vinyl acetate present at the start of the reaction is known. Figure 6.3 depicts the plot of vinyl acetate conversion with during the 4-hour run of the

reaction for a VAE emulsion and a miniemulsion copolymerization run. The final conversion achieved does not show any difference for this particular case. Also, the vinyl acetate conversion in the emulsion occurs slightly faster than that in the miniemulsion. This happens because of the lesser surface area and the decreased presence of ethylene molecules in the vicinity of the monomer droplets in the case of an emulsion, which thereby promotes the faster polymerization of vinyl acetate into the copolymer, thus showing a faster conversion of vinyl acetate during the earlier stages of the reaction.

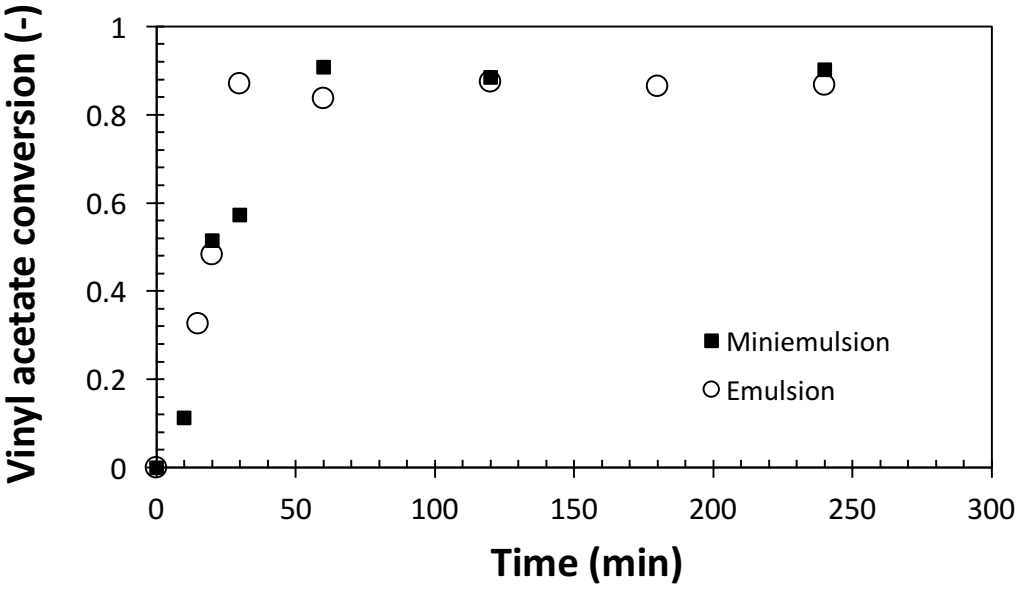


Figure 6.3. Plot of vinyl acetate conversion versus time for an emulsion (ME-VAE 45: 0.159 g-VAc/g-mixture, 80 psig Eth, 0.97% mol-SDS/mol-VAc, 0.31% mol-KPS/mol-VAc, 60°C, 400 rpm) and miniemulsion (MU-VAE 48: 0.159 g-VAc/g-mixture, 80 psig Eth, 1.16% mol-SDS/mol-VAc, 0.50% mol-KPS/mol-VAc, 7.05% mol-HD/mol-VAc, 60°C, 400 rpm) copolymerization runs.

Another interesting result from Figures 6.2 and 6.3 is that although vinyl acetate achieved its maximum monomer conversion of about 87% after first 60 min of the reaction, the ethylene-vinyl acetate molar ratio in the copolymer kept increasing from a value or 0.154 at t = 60 min to 0.244 at t = 240 min without much change in vinyl acetate conversion. Thus it is more likely to find ethylene in the ends of the copolymer molecule in the case of emulsion. The opposite is seen in the case of miniemulsion.

6.3. Particle Size Measurements

Some particle size measurements were taken in order to study the copolymer latex stability of miniemulsions as compared to conventional VAE emulsion copolymers. Figure 6.4 shows the plot of the particle size distributions at two different time points of the same miniemulsion run MU-VAE 17. The first one was taken right after the ultrasonication process but before the start of polymerization while the second measurement was taken after the polymerization run. A decrease of particle size upon ultrasonication has been observed by authors as well [38, 39]. After employing high energy methods, the monomer droplets are broken into smaller droplets and are stabilized by surfactant and further prevent to coalesce with the help of the co-surfactant hexadecane. During polymerization, the curve makes a shift to the right as the polymer particles grow in size.

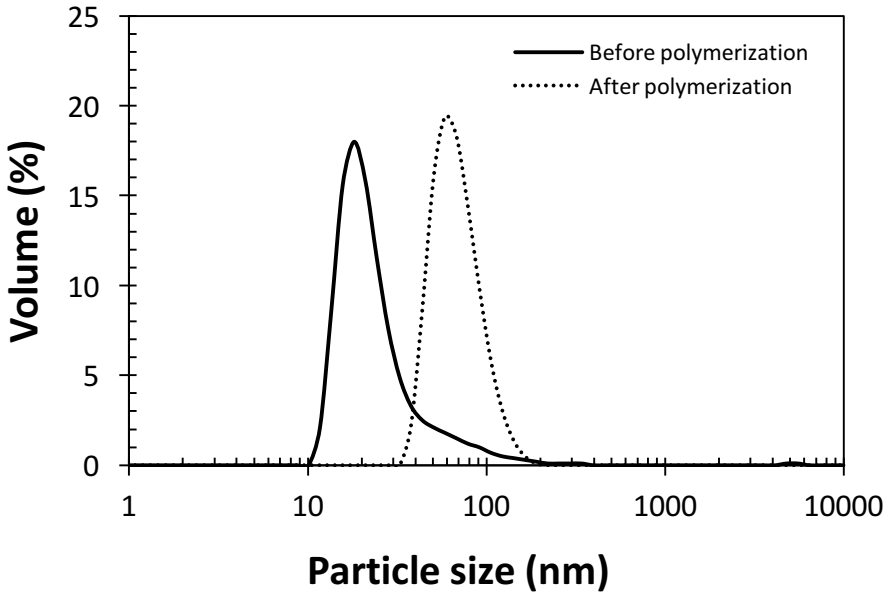


Figure 6.4. Particle size distributions of a miniemulsion run (MU-VAE 17) before and after polymerization.

In order to study the differences in particle stability of miniemulsion latex obtained by both homogenizing and ultrasonication as compared to a conventional emulsion latex, the particle size distributions of two runs MH-VAE 08, MU-VAE 10 are shown in Figure 6.5. There was not much of a difference in mean particle sizes between that of an emulsion and a miniemulsion. While the mean particle size was greater in emulsions for some of the runs, it was lesser than that of miniemulsions in the other runs. However, it could be seen more or less that increase the surfactant to monomer ratio often produced a latex with smaller particle sizes. Although both the miniemulsion methods produce distributions with comparable mean particle sizes of around 113 nm that remained stable two weeks after polymerization, it was observed that

ultrasonication produces a narrower distribution in particle sizes. All high pressure miniemulsion runs were conducted through ultrasonication. In the particle size distributions that follow the high pressure runs, it will be seen that VAE miniemulsions have a greater stability and shelf life in comparison to its emulsion counterparts.

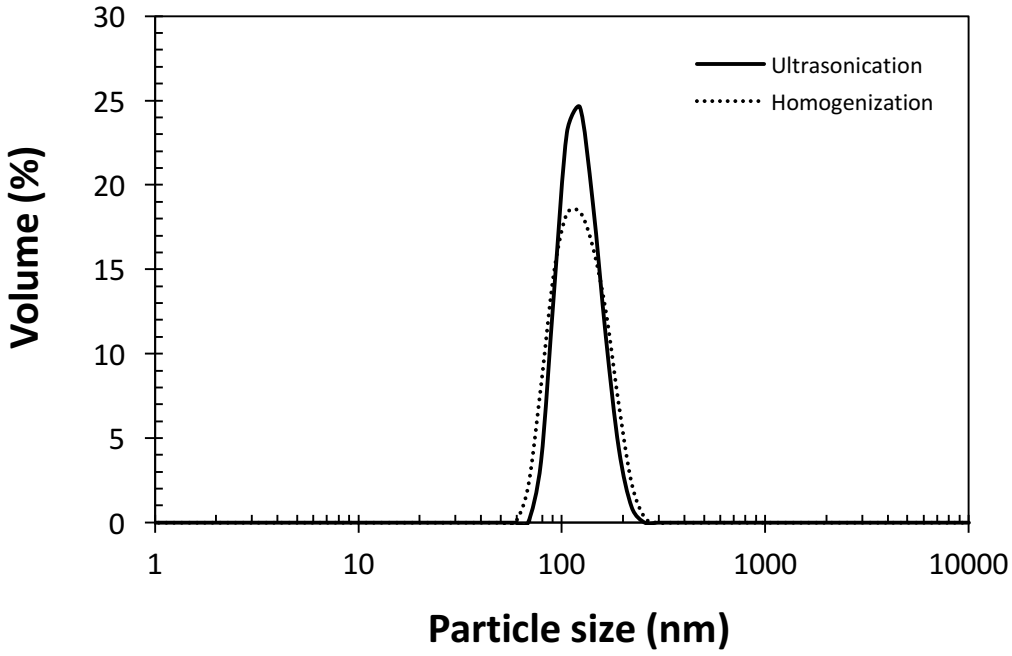


Figure 6.5. Particle size distributions of miniemulsion latexes obtained by ultrasonication and homogenization.

6.4. Viscosity Measurements

For most of the samples, an increase in shear rate brought about a decrease in the viscosity up to a certain value beyond which the viscosity remained constant for any

further increase in shear rates. This constant value of viscosity was taken as the apparent viscosity of the polymer latex. Figure 6.6 shows the differences in viscosity of polymer latexes formed by ultrasonication and homogenizing. Emulsions having a broader size distribution tend to have a lower viscosity [40]. During the lower ranges of shear stress, the viscosity is higher when the emulsion homogenized. But as the shear stress increases, the viscosity of both runs stabilize at the same value of about 2.3 x 10^{-3} Pa.s. It goes to show that irrespective of the high energy shearing method employed to generate the miniemulsion, the viscosities of the miniemulsions generated by homogenizing and ultrasonication are almost the same.

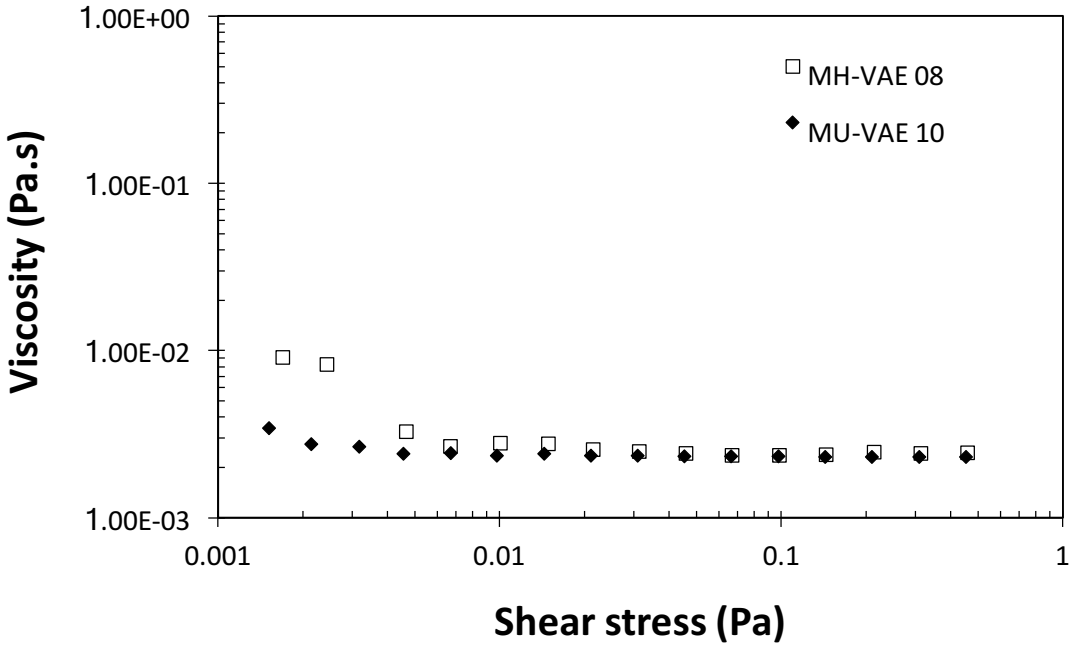


Figure 6.6. Plot of viscosity versus shear stress for miniemulsion latexes formed by ultrasonication and homogenizing.

For most of the samples, an increase in shear rate brought about a decrease in the viscosity up to a certain value beyond which the viscosity remained constant for any further increase in shear rates. This constant value of viscosity was taken as the apparent viscosity of the polymer latex. Viscosity versus shear rate plots for a miniemulsion and emulsion are compared in Figure 6.7. The viscosity of the emulsion is about 2.41 mPa.s while that of the miniemulsion is lower at 1.68 mPa.s. It was found that the latexes produced by miniemulsion polymerization had lower viscosities than those obtained by conventional emulsion polymerization, the reason being the broader particle size distribution as described by some authors [40]. Studies by other authors showed that the viscosity of polymer prepared by conventional emulsion can be as large as 6.5 times higher than the latex obtained using the miniemulsion process [41]. This is because as the mean distance of separation between the droplets decreases, it leads to an increase in hydrodynamic interaction and viscosity. Moreover, due to the quite short nucleation period of conventional emulsion, most of the particles are formed at the same period of time, leading to particles with rather non-homogeneous sizes. In the miniemulsion case, however, the narrow distribution of monomer particle size together with the longer nucleation period leads to such a narrow particle size distribution, which conducts to a lower viscosity. As there was no significant difference particle size distributions of emulsions and miniemulsions in this study, it is concluded that there could be other factors that affect viscosity. Rodrigues and Schork [42] investigated the shear stability of

latexes of similar size produced by miniemulsion and conventional emulsion polymerization. It was found that miniemulsion latexes were more stable than conventional ones.

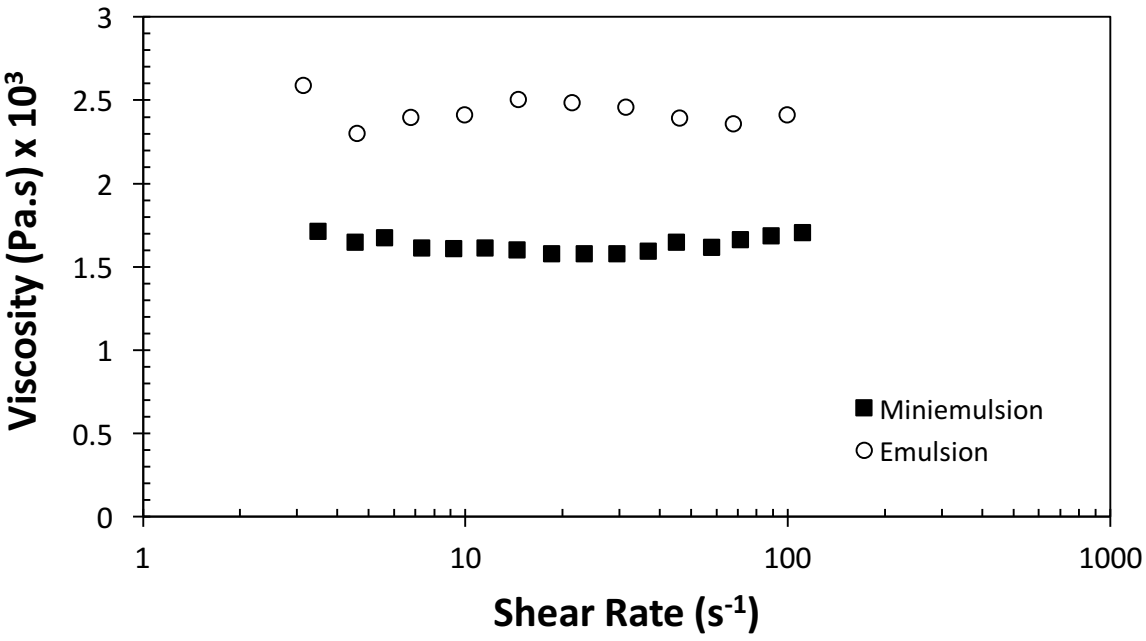


Figure 6.7. Plot of viscosity versus shear rate for a VAE emulsion and miniemulsion copolymer latex.

6.5. High pressure VAE miniemulsion copolymerization

In order to answer the core objective of this research work as to how miniemulsions overcome mass transport limitations especially at higher ethylene partial pressures, runs involving copolymerization at increased pressures were performed to

observe the manner in which ethylene gets incorporated into the copolymer. The reaction conditions used in these high pressure experiments are given in Appendix A.3. ^{1}H NMR spectra of the high pressure miniemulsion runs have been catalogued in Appendix B.2. Table 6.2 that summarizes the calculation ethylene to vinyl acetate ratio and subsequent monomer conversions from the NMR spectra.

Table 6.2. Summary of ^{1}H NMR spectra of samples taken at different ethylene partial pressures for VAE miniemulsion copolymerization

Run	Ethylene partial pressure (psig)	Et/VAc (mol/nol)	Et mol fraction (mol/mol)	VAc mol fraction (mol/mol)	Et wt. fraction (g/g)	VAc wt. fraction (g/g)
MU-VAE 36	100	0.346	0.257	0.743	0.101	0.899
MU-VAE 52	150	0.573	0.364	0.636	0.157	0.843
MU-VAE 38	200	0.796	0.443	0.557	0.206	0.794
MU-VAE 54	250	0.928	0.481	0.519	0.232	0.768
MU-VAE 40	300	1.007	0.502	0.498	0.247	0.753

All measurements taken at the end of reaction at t = 240 min

Figure 6.8 comprehensively summarizes the Et/VAc ratios in all the normal emulsion runs at different ethylene partial pressures. It can be seen that as the partial pressure of ethylene increases, the amount of ethylene getting incorporated into the copolymer shows an increase, similar to what was seen in conventional VAE emulsion.

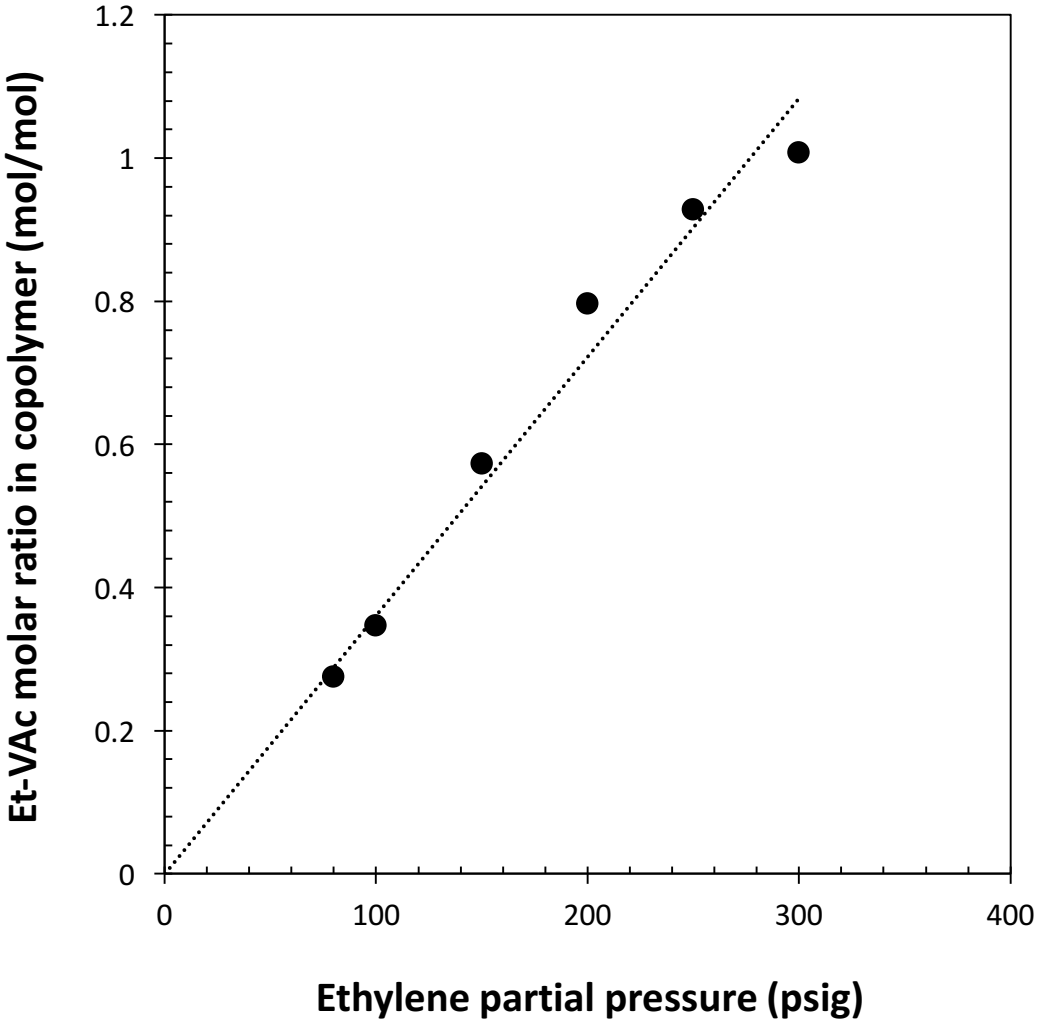
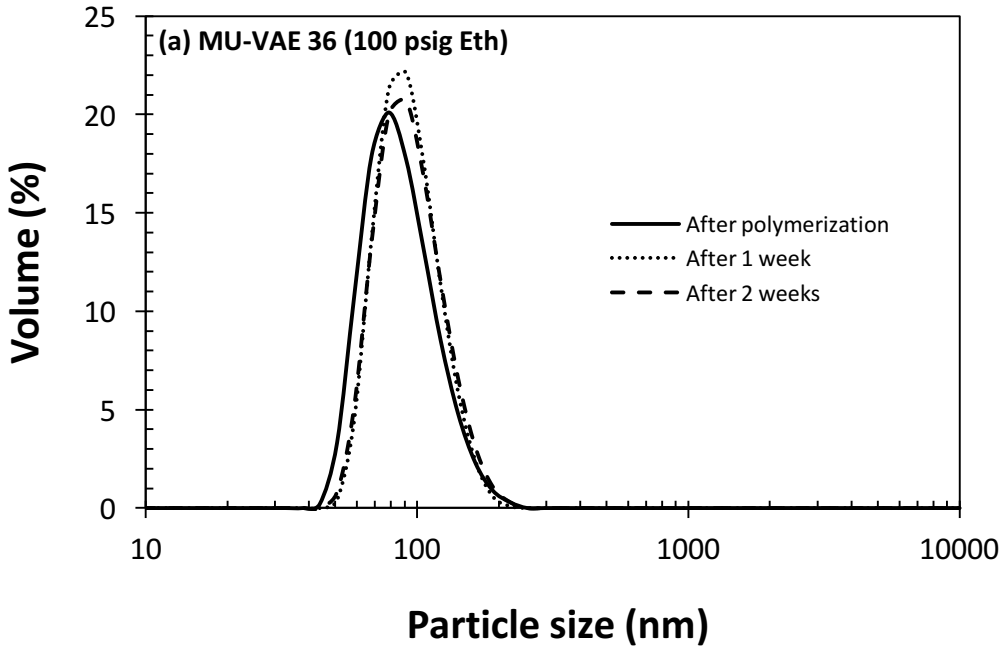
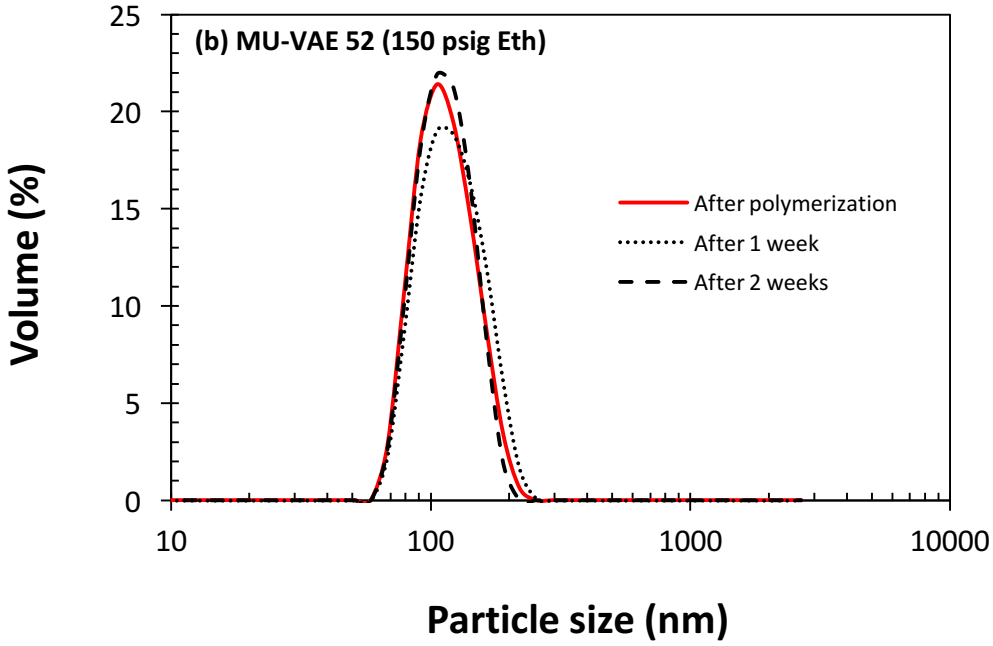
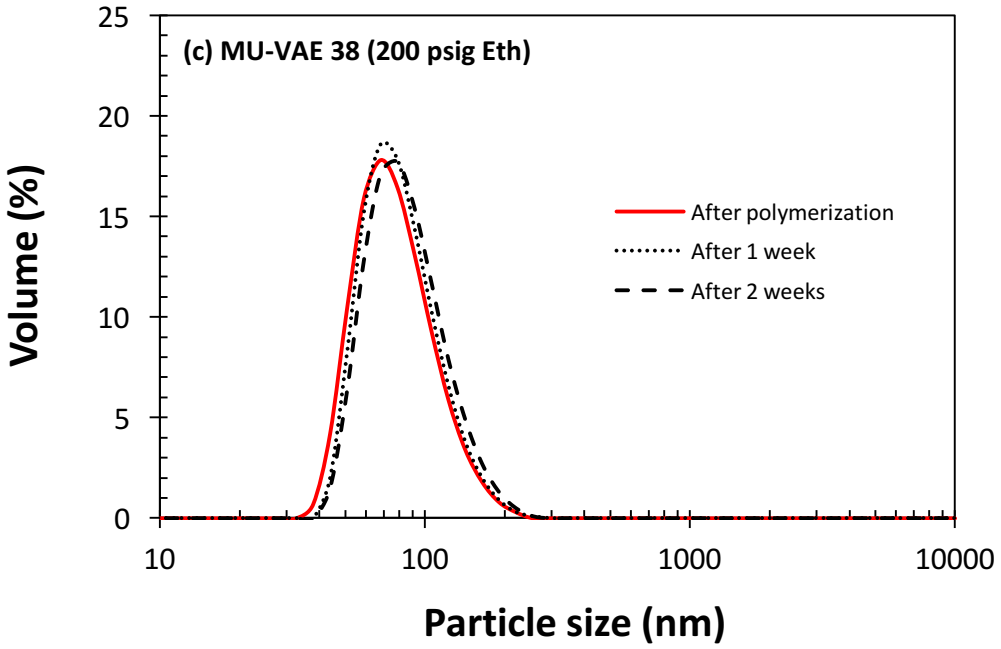


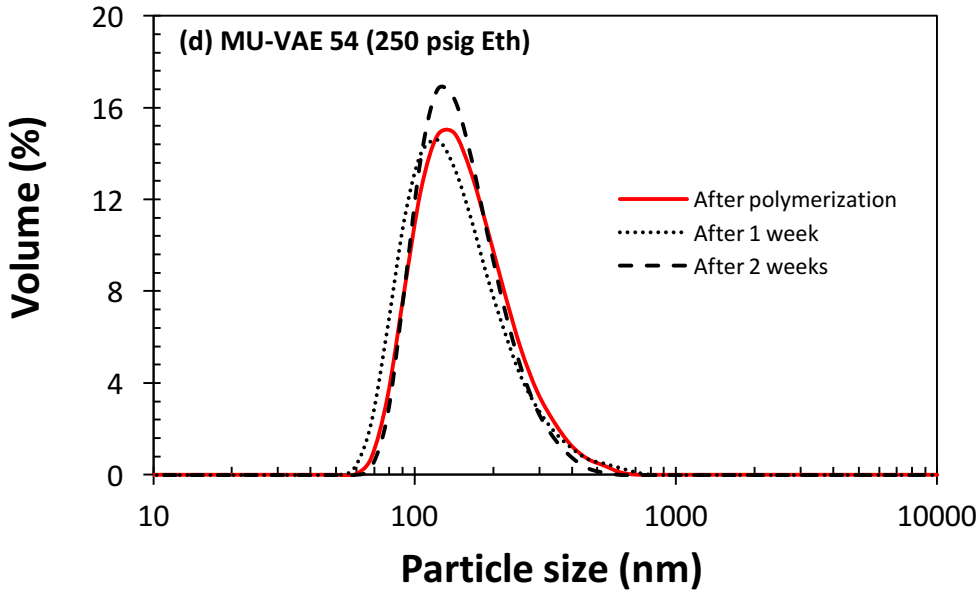
Figure 6.8. Plot of ethylene to vinyl acetate molar ratio in copolymer as a function of ethylene partial pressure (psig) for VAE miniemulsion copolymerization.

Particle size distributions at different ethylene partial pressures were measured right after polymerizations – no pattern was observed as the pressure was increased. Also, miniemulsions show more stability at different ethylene partial pressures as compared to normal emulsions. Figure 6.9 shows the particle size distributions of the above runs and Table 6.3 summarizes the mean particle sizes at different time points for these particle size distributions. Figure 6.10 summarizes the data given in Table 6.3 as it depicts a plot of the variation of mean particle sizes over time.


(a) MU-VAE 36 (100 psig Eth)
Volume (%)
Particle size (nm)
After polymerization
After 1 week
After 2 weeks
0
5
10
15
20
25
10
100
1000
10000


(b) MU-VAE 52 (150 psig Eth)
Volume (%)
Particle size (nm)
After polymerization
After 1 week
After 2 weeks
0
5
10
15
20
25
10
100
1000
10000


(c) MU-VAE 38 (200 psig Eth)
Volume (%)
Particle size (nm)
After polymerization
After 1 week
After 2 weeks
0
5
10
15
20
25
10
100
1000
10000


(d) MU-VAE 54 (250 psig Eth)
Volume (%)
Particle size (nm)
After polymerization
After 1 week
After 2 weeks
0
4
8
12
16
20
10
100
1000
10000

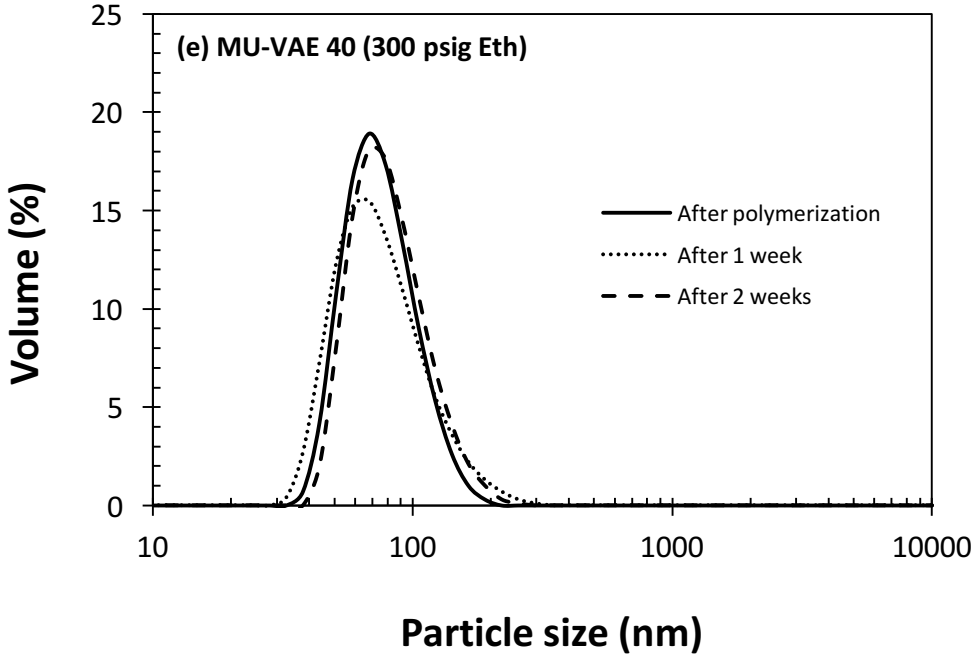


Figure 6.9. Particle size distributions of miniemulsion emulsion VAE copolymerization runs at different ethylene partial pressures taken over a period of 2 weeks corresponding to the following runs (a) MU-VAE 36, (b) MU-VAE 52, (c) MU-VAE 38 (d) MU-VAE 54 and (e) MU-VAE 40.

Table 6.3. Measured mean particle sizes of the distributions of miniemulsions prepared at different ethylene partial pressures

Run	Ethylene partial pressure (psig)	Mean particle size (nm)		
		After polymerization	After 1 week	After 2 weeks
MU-VAE 36	100	100.8	103.5	106.5
MU-VAE 52	150	94.9	98.4	102.7
MU-VAE 38	200	95.0	96.8	103.0
MU-VAE 54	250	103.6	106.2	111.4
MU-VAE 40	300	107.1	98.8	100.8

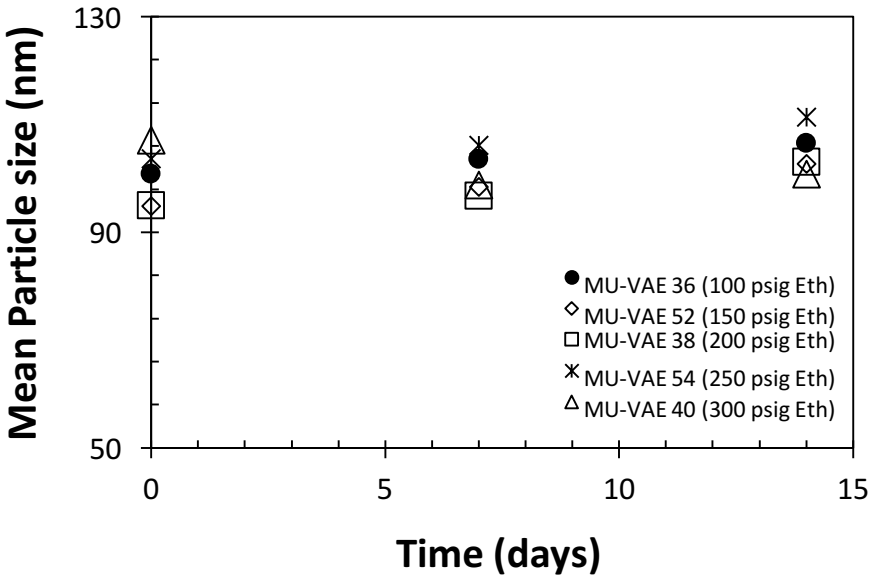


Figure 6.10. Mean particle size (nm) as a function of time (days) of four VAE miniemulsion copolymerization runs on the high pressure reactor at different ethylene partial pressures.

6.6. Estimation of ethylene content in emulsion and miniemulsion droplets

6.6.1. Evaluating reactivity ratios r_1 and r_2

The core of the study involves a method of finding the concentration of ethylene in the vinyl acetate droplets in the monomer phase and see if there is a correlation between the ethylene content with time or vinyl acetate conversion. In order to determine the ethylene to vinyl acetate molar ratio in the monomer mixture from the copolymer compostion data using the Mayo-Lewis equation, the reactivity ratios for vinyl

acetate (r_1) and ethylene (r_2) need to be determined as a first step. Literature concerning the reactivity ratios of vinyl acetate and ethylene measured at different reaction conditions are listed in Table 6.4. Among all the values shown, the reaction conditions of experiments conducted by German and Heikens [43] and Rätzsch et al. [45] match closely to what is done in this study. Erusalimskii et al. [48] found that the reactivity ratios of ethylene and vinyl acetate both increased significantly at 60°C when the pressure was increased from 10 to 120 MPa using ethylene as the monomer. But as far as this study is concerned, the pressure has been raised only to a maximum of 2.76 MPa (400 psig) and hence it can be assumed that reactivity ratios do not change with an increase in ethylene partial pressure. The values of r_1 and r_2 by German and Heikens [43] have been used to theoretically determine the mole fractions of vinyl acetate and ethylene in the monomer phase in this study, since both the temperature and pressure are close to the reaction conditions used in this study.

Table 6.4. Reactivity ratios of vinyl acetate and ethylene under different reaction conditions as determined by various authors

r_1	r_2	Reaction conditions		Author(s)	Reference
		Temperature (°C)	Ethylene partial pressure (psig)		
1.08	1.07	90	14223	Bukhart and Zutty (1963)	[44]
1.37	0.77	60	1470	Rätzsch et al. (1971)	[45]
0.70	0.42	135	4410	Filley et al. (2002)	[46]
1.00	1.01	150	11948	Brown and Ham (1964)	[47]
1.14	0.16	60	1422	Erussalimsky et al. (1967)	[48]
3.70	0.70	60	17068	Erussalimsky et al. (1967)	[48]
1.51	0.74	62	498	German and Heikens (1971)	[43]

6.6.2. Estimation of ethylene content in emulsion and miniemulsion droplets at different time points

The concentration (and not the mole fraction) of ethylene in vinyl acetate at these time points are obtained by knowing the conversion of vinyl acetate at that point in time and the corresponding mole fraction of ethylene in the copolymer. The conversion of vinyl acetate is obtained by using ^{1}H NMR data and gravimetric methods while the mole fraction of ethylene in monomer phase is obtained using Mayo-Lewis equation from the copolymer composition data. ^{1}H NMR data for runs ME-VAE 45 and MU-VAE 48 (catalogued in Appendix A) are used and Table 6.5 and 6.7 depict the corresponding mole fraction values.

Table 6.5. Vinyl acetate and ethylene mole fractions in the copolymer and monomer bulk phase at different time points for a conventional emulsion run at low pressure (80 psig Eth)

Time (min)	Et/VAc (mol/mol in copolymer)	Mole fractions (mol/mol)			
		F_1	F_2	f_1	f_2
15	0.178	0.849	0.151	0.791	0.209
20	0.173	0.853	0.147	0.796	0.204
30	0.154	0.867	0.133	0.814	0.186
120	0.195	0.837	0.163	0.776	0.224
180	0.234	0.810	0.190	0.743	0.257
240	0.244	0.804	0.196	0.735	0.265

F_1 = VAc mole fraction in copolymer; F_2 = Eth mole fraction in copolymer; f_1 = VAc mole fraction in bulk phase; f_2 = Eth mole fraction in bulk phase

Table 6.6. Vinyl acetate and ethylene mole fractions in the copolymer and monomer bulk phase at different time points for a miniemulsion run at low pressure (80 psig Eth)

Time (min)	Et/VAc (mol/mol in copolymer)	Mole fractions (mol/mol)			
		F_1	F_2	f_1	f_2
15	0.603	0.624	0.376	0.534	0.466
30	0.513	0.661	0.339	0.573	0.427
45	0.470	0.680	0.320	0.593	0.407
60	0.383	0.723	0.277	0.641	0.359
120	0.333	0.750	0.250	0.671	0.329
240	0.355	0.738	0.262	0.658	0.342

F_1 = VAc mole fraction in copolymer; F_2 = Eth mole fraction in copolymer; f_1 = VAc mole fraction in bulk phase; f_2 = Eth mole fraction in bulk phase

Figure 6.11 depicts the ethylene mole fraction in the copolymer (F_2) at different time points for an emulsion and a miniemulsion. It can be seen clearly that miniemulsion has a higher ethylene content overall. Both the emulsion and miniemulsion data points initially show a dip indicating a higher vinyl acetate incorporation during this phase followed by a gradual increase indicating ethylene transition from monomer phase into the copolymer. Even from the reactivity ratios for both the comonomers used in the study as well as by the other authors, it can be noted that r_1 is always greater than r_2, indicating a higher preference of the copolymer towards VAc than towards Eth. Note that this does not mean that ethylene is completely ignored, but is just less preferred. Thus, during the initial stages of the reaction when both the comonomers are available in abundance, vinyl acetate will be preferred. But since these are semibatch reactions where vinyl acetate is limited and ethylene is continuously supplied, the ethylene mole fraction in the copolymer starts to rise upon depletion of VAc.

Figure 6.12 depicts the plot of ethylene mole fraction in the monomer phase as function of time. The plots in Figures 6.11 and 6.12 are very similar indicating that a high ethylene mole fraction in the monomer phase corresponds to a high ethylene incorporation in the copolymer phase, and vice versa. The concentration of ethylene in the monomer phase is higher for the miniemulsion indicating that the ethylene molecules have overcome this mass transport limitation and presented itself in the vicinity of sites where polymerization takes place.

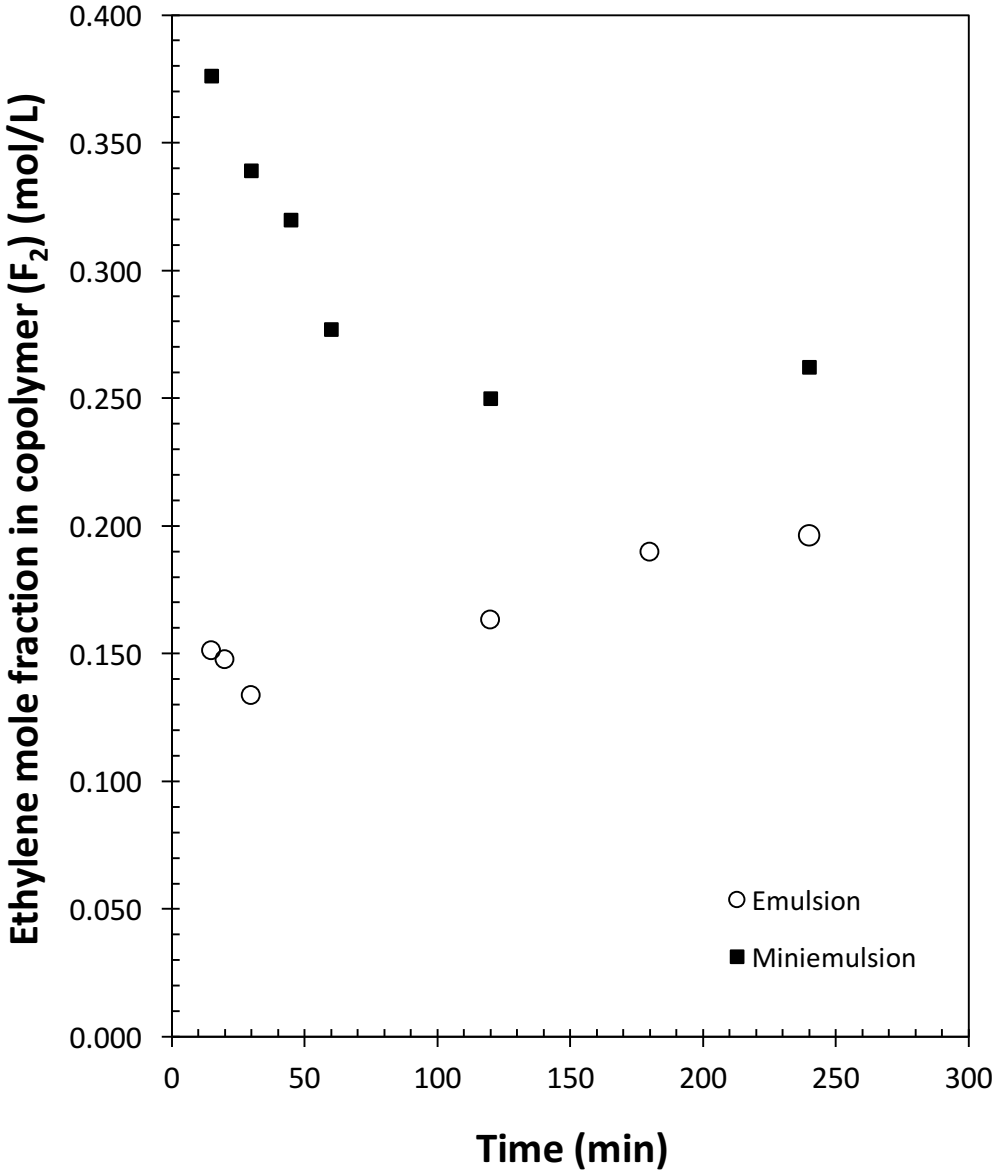


Figure 6.11. Plot of ethylene mole fraction in copolymer at different time points for both VAE emulsion (ME-VAE 45: 0.159 g-VAc/g-mixture, 80 psig Eth, 0.97% mol-SDS/mol-VAc, 0.31% mol-KPS/mol-VAc, 60°C, 400 rpm) and miniemulsion (MU-VAE 48: 0.159 g-VAc/g-mixture, 80 psig Eth, 1.16% mol-SDS/mol-VAc, 0.50% mol-KPS/mol-VAc, 7.05% mol-HD/mol-VAc, 60°C, 400 rpm) copolymerization runs.

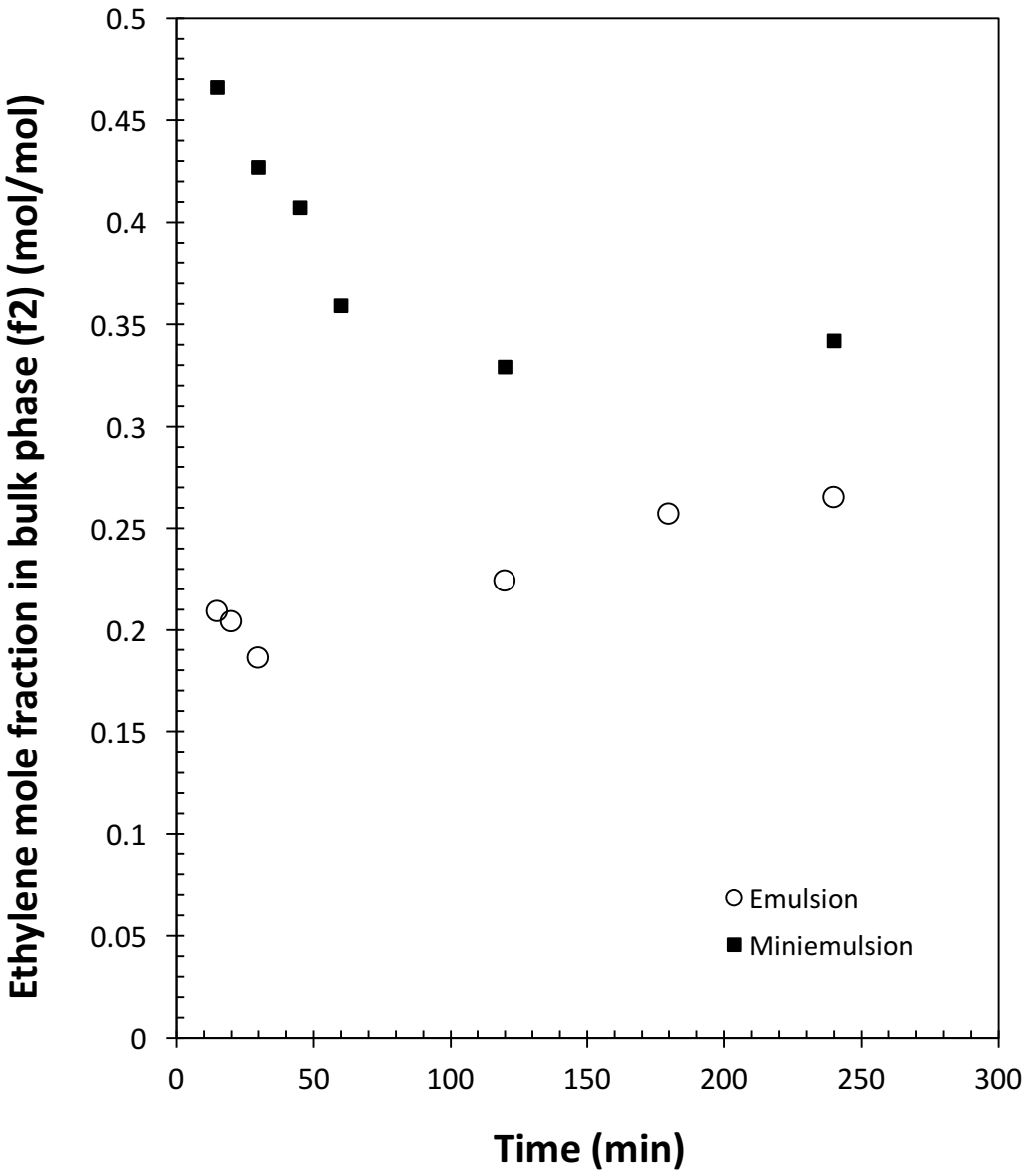


Figure 6.12. Plot of ethylene mole fraction in the bulk phase at different time points for both VAE emulsion (ME-VAE 45: 0.159 g-VAc/g-mixture, 80 psig Eth, 0.97% mol-SDS/mol-VAc, 0.31% mol-KPS/mol-VAc, 60°C, 400 rpm) and miniemulsion (MU-VAE 48: 0.159 g-VAc/g-mixture, 80 psig Eth, 1.16% mol-SDS/mol-VAc, 0.50% mol-KPS/mol-VAc, 7.05% mol-HD/mol-VAc, 60°C, 400 rpm) copolymerization runs.

Figure 6.13 shows the mass of ethylene in grams incorporated into the copolymer per gram of the monomer mixture that includes both the organic VAc monomer phase and the aqueous phase, as a function of time. Although the ethylene mole fraction shows a dip during the initial stages of the reaction as seen in Figure 6.12, the absolute amount of ethylene incorporated into VAE copolymer shows an increase for both the emulsion and miniemulsion. It is evident that the amount of ethylene incorporated in a miniemulsion run is much more than incorporated in a normal emulsion run. Figure 6.14 depicts the dependence of ethylene concentration (and not mole fraction) in the vinyl acetate monomer droplets versus time for the same experimental runs ME-VAE 45 and MU-VAE 48. Both show a decrease over time because the absolute concentration of vinyl acetate decreases over the course of the polymerization and therefore the absolute concentration of ethylene dissolved in it will also show a decrease. The concentration of ethylene is much higher in a miniemulsion, until the very end where the ethylene concentration in the emulsion is slightly higher. This is because of the slightly higher vinyl acetate conversion in miniemulsion which leads to a decreased absolute concentration of VAc, which in turn leads to a decreased ethylene concentration in VAc. Figure 6.15 shows a plot of the same ethylene concentration in monomer phase, but this time as a function of vinyl acetate concentration. A trend can be observed in both cases where it becomes possible to track and predict the ethylene concentration, given the time or the vinyl acetate conversion. Figure 6.15 gives a fairly good idea about what takes place during the

first 60 minutes of the reaction because that is when most of the vinyl acetate conversion takes place.

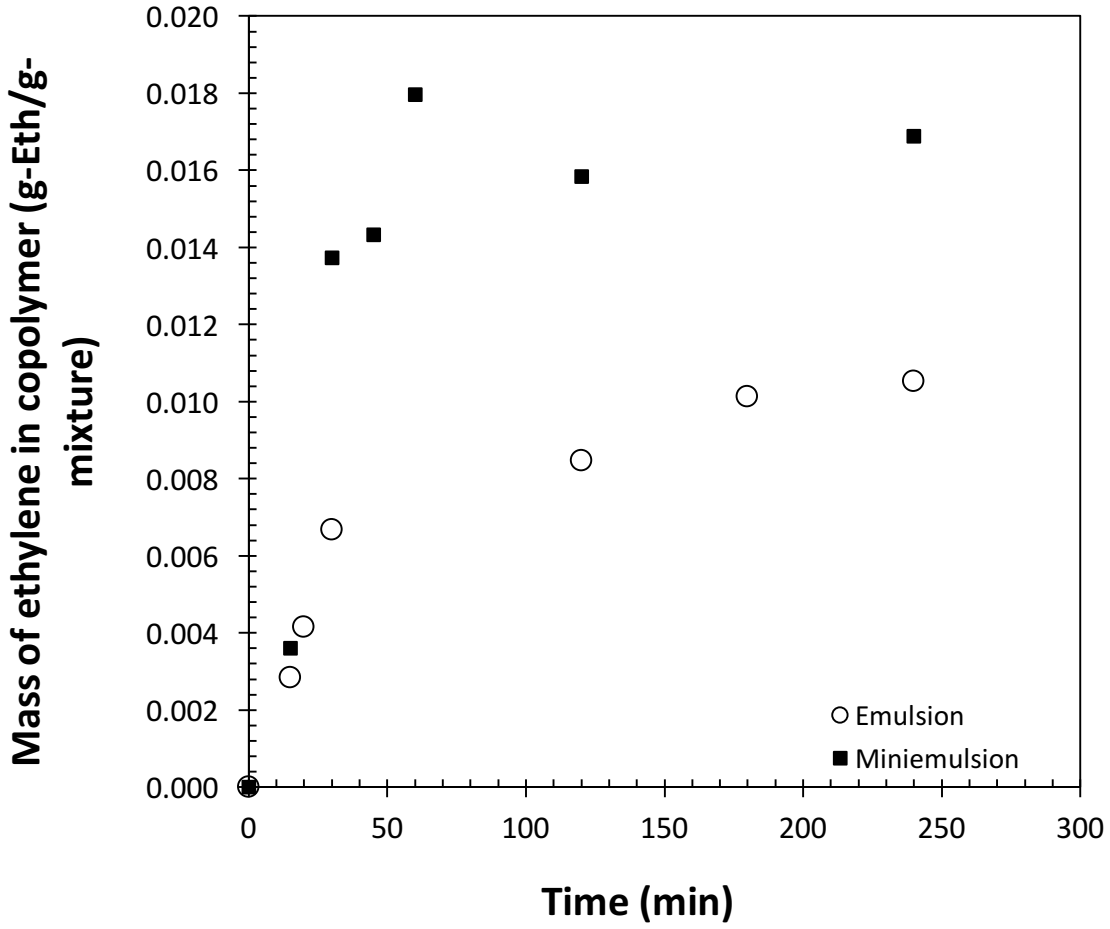


Figure 6.13. Plot of mass of ethylene (g-Eth/g-mixture) incorporated into the copolymer as a function of time (min) for VAE emulsion (ME-VAE 45: 0.159 g-VAc/g-mixture, 80 psig Eth, 0.97% mol-SDS/mol-VAc, 0.31% mol-KPS/mol-VAc, 60°C, 400 rpm) and miniemulsion (MU-VAE 48: 0.159 g-VAc/g-mixture, 80 psig Eth, 1.16% mol-SDS/mol-VAc, 0.50% mol-KPS/mol-VAc, 7.05% mol-HD/mol-VAc, 60°C, 400 rpm) copolymerization runs.

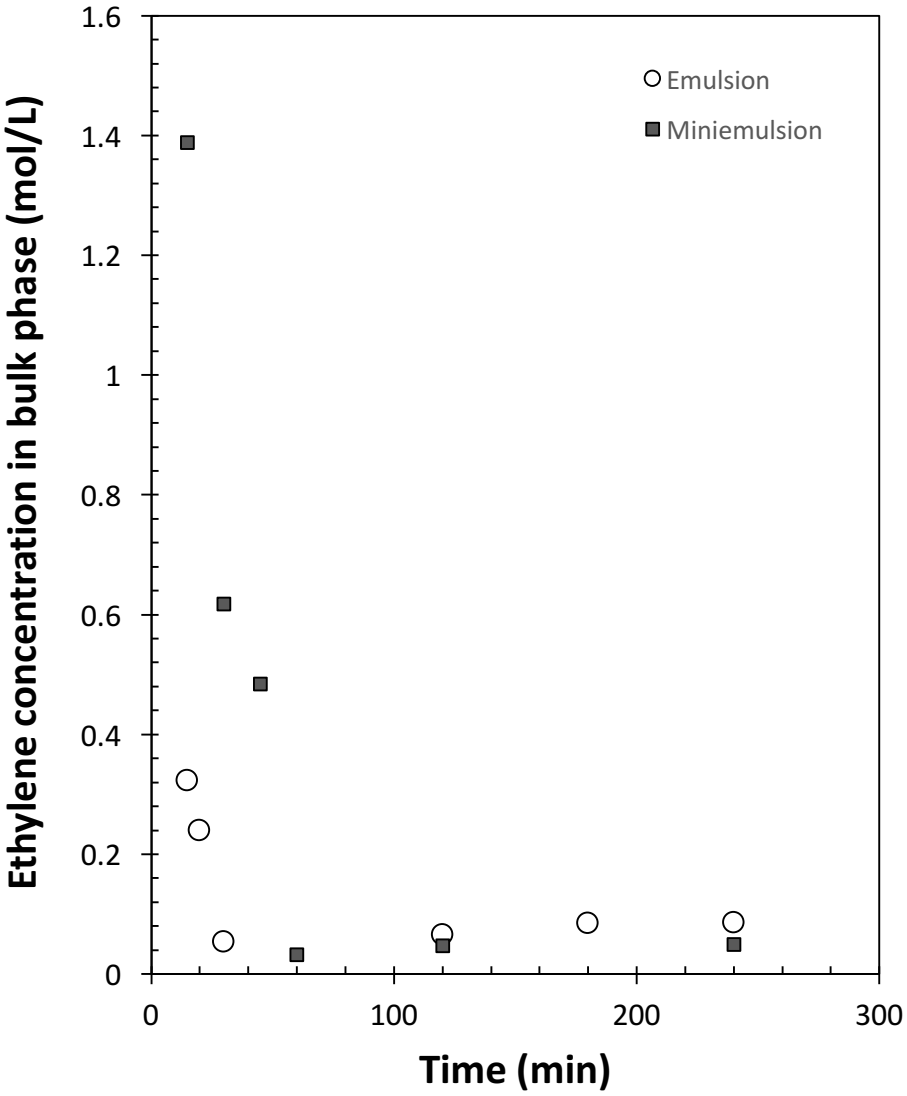


Figure 6.14. Plot of ethylene concentration (mol/L) in the bulk phase as a function of reaction time (min) for both VAE emulsion (ME-VAE 45: 0.159 g-VAc/g-mixture, 80 psig Eth, 0.97% mol-SDS/mol-VAc, 0.31% mol-KPS/mol-VAc, 60°C, 400 rpm) and miniemulsion (MU-VAE 48: 0.159 g-VAc/g-mixture, 80 psig Eth, 1.16% mol-SDS/mol-VAc, 0.50% mol-KPS/mol-VAc, 7.05% mol-HD/mol-VAc, 60°C, 400 rpm) copolymerization runs.

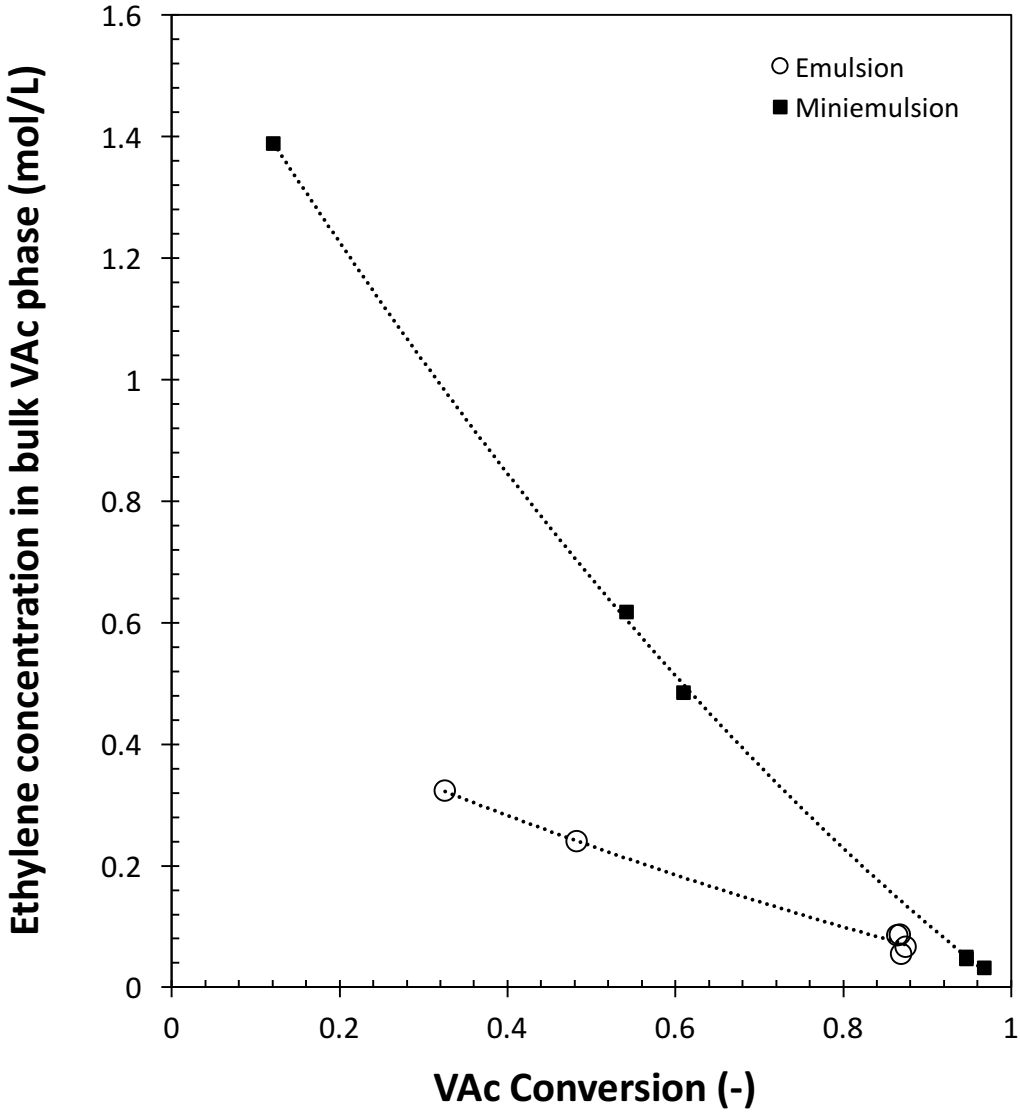


Figure 6.15. Plot of ethylene concentration (mol/L) in the bulk phase as a function of vinyl acetate conversion (-) for both VAE emulsion (ME-VAE 45: 0.159 g-VAc/g-mixture, 80 psig Eth, 0.97% mol-SDS/mol-VAc, 0.31% mol-KPS/mol-VAc, 60°C, 400 rpm) and miniemulsion (MU-VAE 48: 0.159 g-VAc/g-mixture, 80 psig Eth, 1.16% mol-SDS/mol-VAc, 0.50% mol-KPS/mol-VAc, 7.05% mol-HD/mol-VAc, 60°C, 400 rpm) copolymerization runs.

6.6.3. Obtaining ethylene concentration in bulk phase at different ethylene partial pressures

Table 6.7 lists the values of mole fractions of ethylene and vinyl acetate at the end of the reaction run (t = 240 minutes) in both the copolymer as well as in the organic monomer phase using the Mayo-Lewis equation and the calculated reactivity ratios. Since samples could not be taken from the high pressure reactor at different time points, the incorporation of ethylene could not be tracked at different time points for each experiment. In Table 6.7, Et/VAc refers to the ratio of ethylene to vinyl acetate in the copolymer phase measured by ^{1}H NMR, F_1 is the vinyl acetate mole fraction in copolymer, F_2 (= 1 - F_1) is the ethylene mole fraction in copolymer, f_1 is the vinyl acetate mole fraction in bulk phase and f_2 (= 1 - f_1) is the ethylene mole fraction in bulk phase.

Table 6.7. Vinyl acetate and ethylene mole fractions in the copolymer and monomer bulk phase at different ethylene partial pressures for an emulsion

Ethylene partial pressure (psig)	Et/VAc (mol/mol in copolymer)	Mole fractions (mol/mol)			
		F_1	F_2	f_1	f_2
80	0.244	0.804	0.196	0.833	0.167
100	0.281	0.781	0.219	0.810	0.190
150	0.550	0.645	0.355	0.683	0.317
200	0.575	0.588	0.412	0.586	0.414
250	0.888	0.530	0.470	0.530	0.470
300	0.956	0.511	0.489	0.489	0.511

F_1 = VAc mole fraction in copolymer; F_2 = Et mole fraction in copolymer; f_1 = VAc mole fraction in bulk phase; f_2 = Et mole fraction in bulk phase. All measurements taken at the end of reaction (t = 240 min).

Table 6.8. Vinyl acetate and ethylene mole fractions in the copolymer and monomer bulk phase at different ethylene partial pressures for a miniemulsion

Ethylene partial pressure (psig)	Et/VAc (mol/mol in copolymer)	Mole fractions (mol/mol)			
		F_1	F_2	f_1	f_2
80	0.275	0.784	0.216	0.813	0.187
100	0.346	0.743	0.257	0.769	0.231
150	0.573	0.636	0.364	0.646	0.354
200	0.796	0.557	0.443	0.547	0.453
250	0.928	0.519	0.481	0.499	0.501
300	1.007	0.498	0.502	0.473	0.527

F_1 = VAc mole fraction in copolymer; F_2 = Et mole fraction in copolymer; f_1 = VAc mole fraction in bulk phase; f_2 = Et mole fraction in bulk phase. All measurements taken at the end of reaction (t = 240 min).

Figure 6.16 shows the plot of ethylene mole fraction in the copolymer versus that in the monomer phase. The graph y = x is also plotted for reference. As shown in Figure 2.2, this plot resembles a typical plot where $r_1 > 1$, $r_2 < 1$.

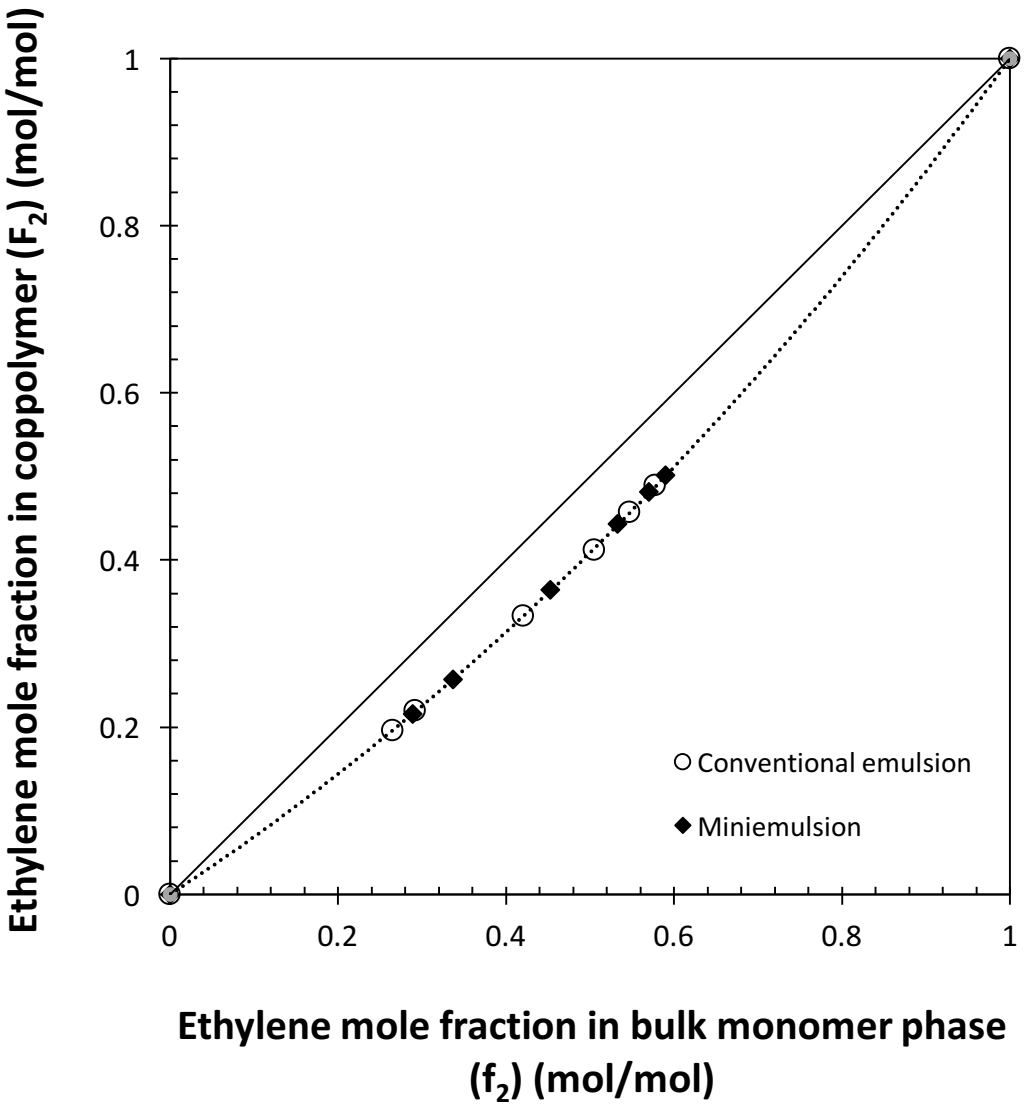


Figure 6.16. Plot of ethylene mole fraction in copolymer phase versus ethylene mole fraction in bulk monomer phase for both VAE emulsion and miniemulsion copolymerization runs.

Figure 6.17 is the superimposition of the plots in Figure 5.9 and Figure 6.8 into one plot to study and compare the differences in the amount of ethylene incorporated at different partial pressures in a miniemulsion and conventional emulsion runs. For a given pressure of ethylene, the miniemulsion runs have a higher ethylene mole fraction in the copolymer phase than the corresponding normal emulsion runs. Once the molar ratios of ethylene to vinyl acetate in the bulk phase have been calculated using the Mayo-Lewis equation, a plot of this mole fraction (f_2) versus ethylene partial pressure has also been studied and plotted in Figure 6.18. It can be observed that as the partial pressure of ethylene increases, the ethylene mole fraction in the bulk phase also increases for both emulsion and miniemulsion. The miniemulsion has almost the same or slightly higher mole fraction of ethylene in the bulk phase than the normal emulsion. It must be noted that the values plotted in Figure 6.18 are estimated and not experimentally measured and that there may be deviations, making it hard to arrive at a conclusion. It is possible that a higher mole fraction of ethylene in the monomer phase resulted in a higher ethylene mole fraction in the copolymer phase due to increased presence in the vicinity of the growing polymer chain. This increased presence of ethylene around the polymerization sites is possible only when ethylene molecules overcomes the mass transport limitations and reach the polymerization loci. With all the experimental data shown till now, there is sufficient evidence that this possible in VAE minimeulsion copolymerization. The conclusions for Chapter 6 are combined with the conclusions and future work section as part of Chapter 7.

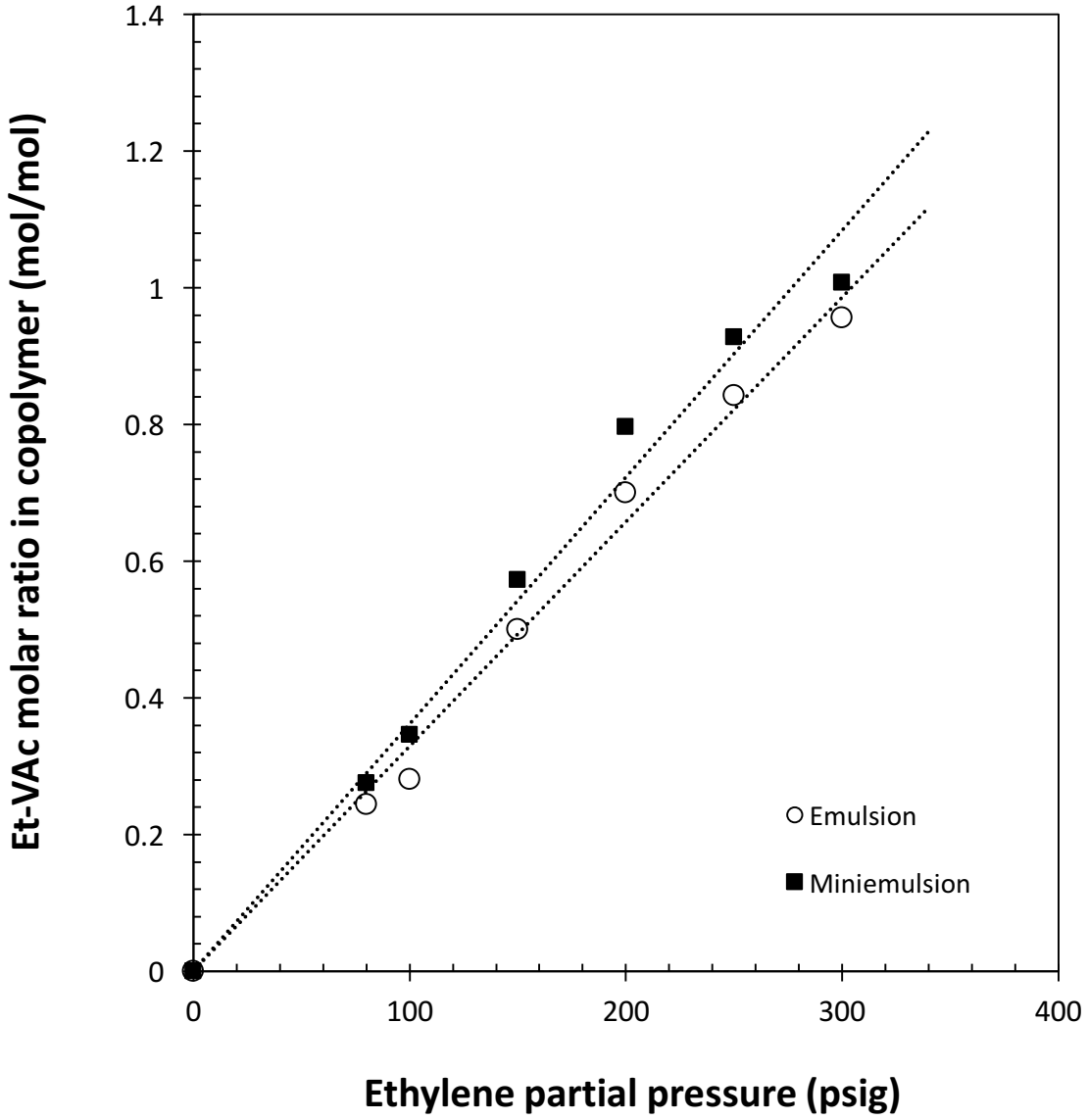


Figure 6.17. Plot of ethylene mole fraction in copolymer at different ethylene partial pressures for both VAE emulsion and miniemulsion copolymerization runs.

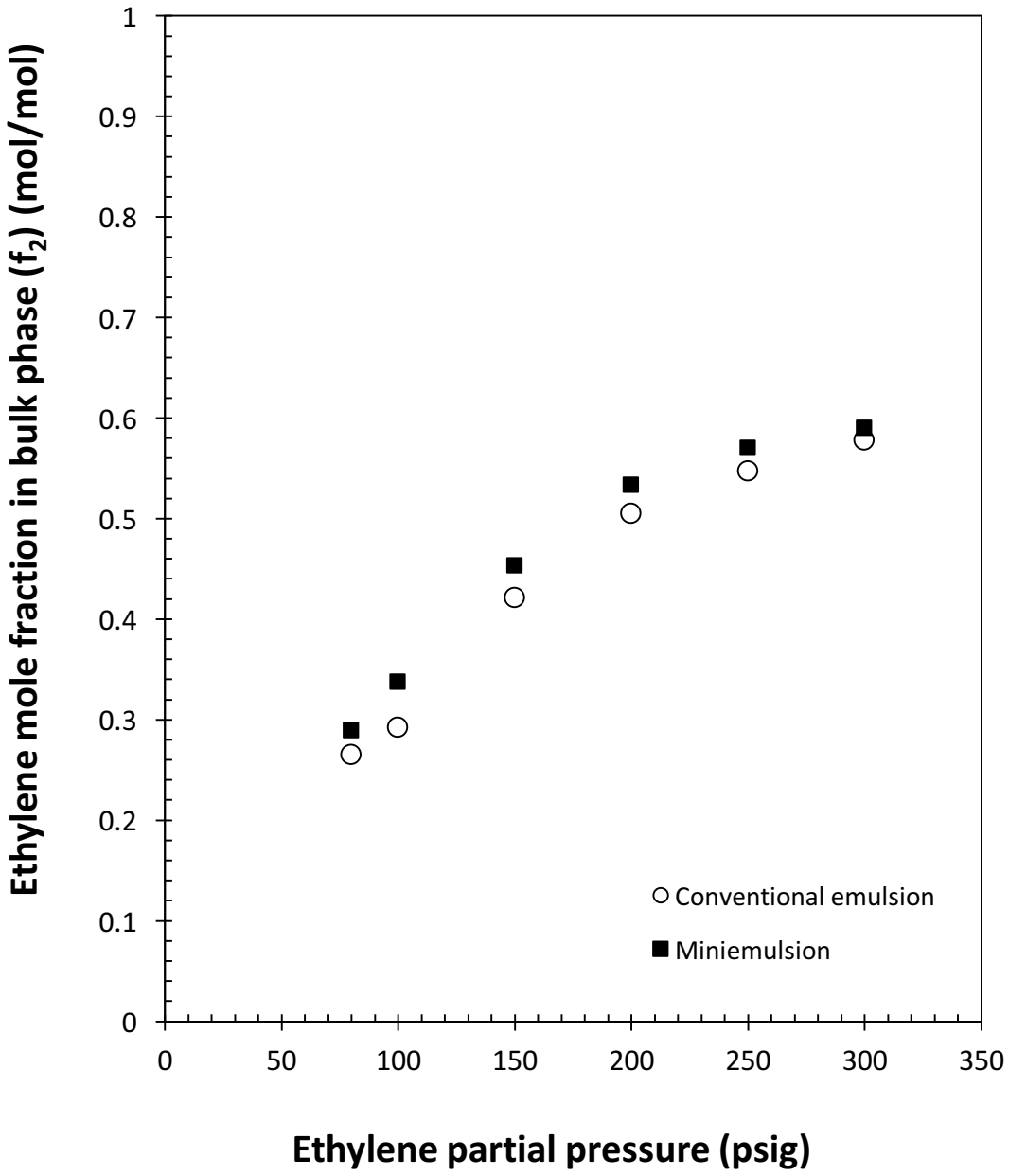


Figure 6.18. Plot of ethylene mole fraction in bulk monomer mixture at different ethylene partial pressures for both VAE conventional emulsion and miniemulsion copolymerization runs.

CHAPTER 7

CONCLUSIONS AND FUTURE WORK

1) General Conclusions

Droplet nucleation is the distinctive feature of miniemulsion polymerization that allows dealing with hydrophobic reactants because the need for mass transfer through the aqueous phase is minimized in miniemulsion polymerization. Conventional semi-batch emulsion copolymerization of vinyl acetate and ethylene is controlled by the monomer transfer from the droplets to the polymerization locus through the aqueous phase, which greatly limits the incorporation of water insoluble ethylene. In contrast, miniemulsion copolymerization does not involve the diffusion of ethylene molecules across the aqueous phase to the polymerization loci. Its unique droplet nucleation mechanism allows for much higher ethylene incorporation into the copolymer.

2) Stability and properties

In terms of particle sizes, VAE miniemulsion copolymer latexes were much more stable than their conventional emulsion counterparts made under similar reaction conditions. Some VAE miniemulsion latexes remained without much change in mean particle size for over 8 weeks. The particle size distribution of a miniemulsion generated by ultrasonication was narrower than that generated by homogenization. This was true in both VAc homo-polymerization as well as VAE copolymerization. Miniemulsions tended

to be less viscous than emulsions produced under similar conditions. An increase in the monomer concentration brought about an increase in the total solids content and the viscosity.

3) Ethylene concentration

As the ethylene partial pressure was increased from 100 psig to 300 psig, the amount of ethylene incorporated in the copolymer when the reaction run completed also increased. The increase was more in the case of miniemulsion as compared to that in a normal emulsion. The increased incorporation of ethylene in the miniemulsion was due to the increased presence of ethylene around the sites where polymerization took place. This increased presence of ethylene around the polymerization sites is possible only if the ethylene molecules ferry themselves through the aqueous phase overcoming the mass transport limitations. Thus, an increased presence of ethylene in the miniemulsion copolymer latex corresponds to decreased mass transfer limitations in a miniemulsion as compared to that in an emulsion. These arguments go in to show that miniemulsion is indeed a better alternative to produce VAE copolymers with increased ethylene content. The ethylene content in the copolymer and bulk phase can be tracked and predicted as a function of time and vinyl acetate conversion.

4) Future Work

All the results presented in this study so far are from semibatch experiments where ethylene was continuously fed to the reactor. As part of future work, some batch

runs can be carried out where the overhead pressure is monitored with respect to time. Glass transition temperature, one of the very crucial properties of a polymer, can be investigated via differential scanning calorimetry (DSC) for a VAE miniemulsion and emulsion. SEM images of a both emulsion and miniemulsions would provide some useful data on particle sizes and morphologies. Molecular weight distribution data will also be obtained via gel permeation chromatography (GPC) to study further differences between VAE emulsions and miniemulsions. The tracking of ethylene concentration at different time points was done only at lower pressures because sampling at different time points could not be done at higher pressures. By sampling and analyzing this data, one could predict the ethylene concentration at any partial pressure for both emulsions and miniemulsions.

Appendix A. Recipe and reaction conditions for each experiment presented in the study.

Appendix A.1. Recipe and reaction conditions for each experiment presented in the study involving emulsion and miniemulsion VAc homo-polymerization

Run no.	Emulsion type*	Water (mol)	VAc (mol)	Wt% of VAc in monomer mixture (g-VAc/g-mixture)	SDS % (mol/mol VAc)	KPS % (mol/mol VAc)	HD% (mol/mol VAc)
ME-VAc 01	E	8.89	0.37	0.166	0.94	0.50	-
MH-VAc 02	H	8.89	0.37	0.166	0.94	0.50	4.49
ME-VAc 03	E	6.11	0.46	0.265	1.40	0.50	-
MH-VAc 05	H	6.11	0.46	0.265	1.40	0.50	4.64
ME-VAc 06	E	6.11	0.46	0.265	1.40	0.50	-
ME-VAc 08	E	12.22	0.37	0.126	3.45	1.22	-
ME-VAc 11	E	6.11	0.46	0.265	1.40	1.00	-
ME-VAc 12	E	6.11	0.46	0.265	2.01	1.00	-
ME-VAc 14	E	8.89	0.37	0.166	0.94	0.50	-
MH-VAc 16	H	8.89	0.37	0.166	0.94	0.50	4.49
ME-VAc 17	E	6.11	0.46	0.265	1.39	0.50	-
MH-VAc 19	H	6.11	0.46	0.265	1.40	0.50	4.64
ME-VAc 20	E	6.11	0.46	0.265	1.40	0.50	-
ME-VAc 26	E	11.67	0.37	0.132	3.73	1.22	-
ME-VAc 27	E	6.11	0.46	0.265	1.40	1.00	-

All experiments were conducted at 60°C, 400 rpm. HD was added only in miniemulsion runs.

* E- Conventional emulsion, U- Miniemulsion by ultrasonication, H- Miniemulsion by homogenization

Appendix A.2. Recipe and reaction conditions for each experiment presented in this study involving VAE emulsion copolymerization

Run no.	Reactor type *	Water (mol)	VAc (mol)	Wt% VAc in monomer mixture (g-VAc/g-mixture)	SDS % (mol/mol VAc)	KPS % (mol/mol VAc)	Ethylene partial pressure (psig)
ME-VAE 43	Lo	8.33	0.33	0.159	0.92	0.31	80
ME-VAE 45	Lo	8.33	0.33	0.159	0.97	0.31	80
ME-VAE 04	Lo	6.11	0.46	0.263	1.40	0.50	90
ME-VAE 05	Lo	6.11	0.56	0.305	1.13	0.40	90
ME-VAE 06	Lo	6.11	0.67	0.344	0.95	0.34	90
ME-VAE 07	Lo	6.11	0.78	0.379	0.82	0.29	90
ME-VAE 49	Lo	6.11	0.46	0.263	1.40	0.50	90
ME-VAE 50	Lo	6.11	0.56	0.305	1.13	0.40	90
ME-VAE 35	Hi	21.11	0.76	0.147	0.97	0.31	100
ME-VAE 51	Hi	21.11	0.76	0.147	0.97	0.31	150
ME-VAE 37	Hi	21.11	0.76	0.147	0.97	0.31	200
ME-VAE 18	Hi	21.11	0.78	0.151	0.97	0.30	200
ME-VAE 53	Hi	21.11	0.76	0.147	0.97	0.31	250
ME-VAE 39	Hi	21.11	0.76	0.147	0.92	0.31	300

* Lo- Low pressure reactor, Hi- High pressure reactor.

All experiments were conducted at 60°C. Agitation: 400 rpm in low pressure reactor, 700 rpm in high pressure reactor.

Appendix A.3. Recipe and reaction conditions for each experiment presented in this study involving VAE miniemulsion copolymerization

Run no.	Emulsion type and reactor *		Water (mol)	VAc (mol)	Wt% VAc in monomer mixture (g-VAc/g-mixture)	SDS % (mol/mol VAc)	KPS % (mol/mol VAc)	HD % (mol/mol VAc)	Ethylene pressure (psig)
MU-VAE 43	U	Lo	8.33	0.16	0.084	0.78	0.50	7.05	80
MU-VAE 44	U	Lo	8.33	0.16	0.084	0.97	0.50	7.05	80
MU-VAE 46	U	Lo	8.33	0.33	0.159	1.16	0.50	7.05	80
MU-VAE 48	U	Lo	8.33	0.33	0.159	1.16	0.50	7.05	80
MH-VAE 08	H	Lo	6.11	0.46	0.265	1.01	0.40	3.07	100
MU-VAE 10	U	Lo	6.11	0.46	0.265	1.01	0.40	3.07	100
MU-VAE 17	U	Lo	6.11	0.46	0.265	1.01	0.40	3.02	100
MU-VAE 55	U	Lo	6.11	0.46	0.265	1.01	0.40	3.07	100
MU-VAE 36	U	Hi	21.11	0.76	0.147	0.79	0.50	6.98	100
MU-VAE 52	U	Hi	21.11	0.76	0.147	0.78	0.50	6.98	150
MU-VAE 38	U	Hi	21.11	0.76	0.147	0.79	0.50	6.98	200
MU-VAE 54	U	Hi	21.11	0.76	0.147	0.78	0.50	6.98	250
MU-VAE 40	U	Hi	21.11	0.76	0.147	0.78	0.50	6.98	300

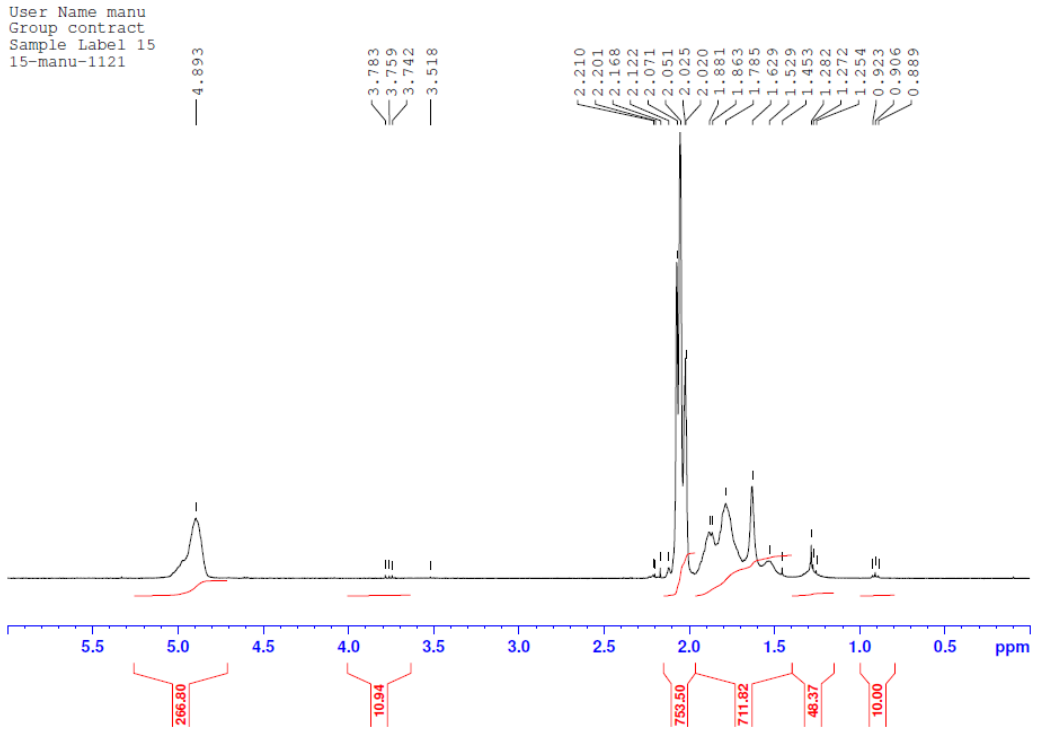
* U- Miniemulsion by ultrasonication, H- Miniemulsion by homogenization, Lo- Low pressure reactor, Hi- High pressure reactor. All experiments were conducted at temperature of 60°C and agitation of 400 rpm in low pressure reactor and 700 rpm in high pressure reactor.

Appendix B. ^{1}H NMR data at different time points for VAE emulsion and miniemulsion runs

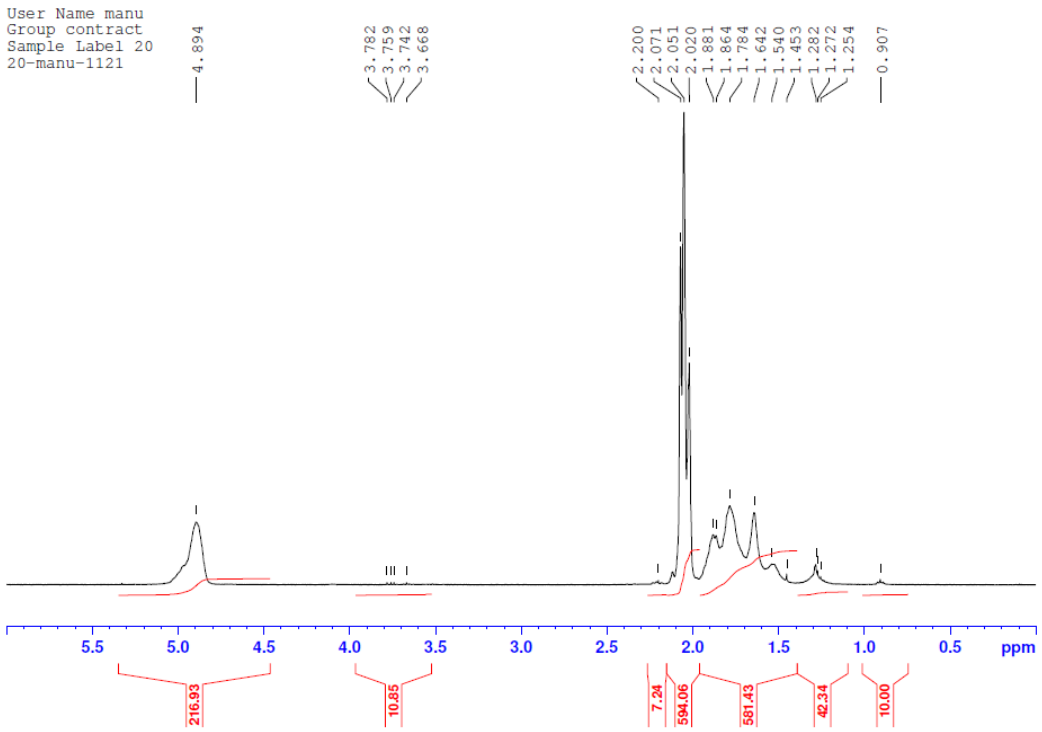
Appendix B.1. Emulsion run ME-VAE 45

Run no.	Reactor type *	Water (mol)	VAc (mol)	Wt% VAc in monomer mixture (g-VAc/g-mixture)	SDS % (mol/mol VAc)	KPS % (mol/mol VAc)	Ethylene partial pressure (psig)
ME-VAE 45	Lo	8.33	0.33	0.159	0.97	0.31	80

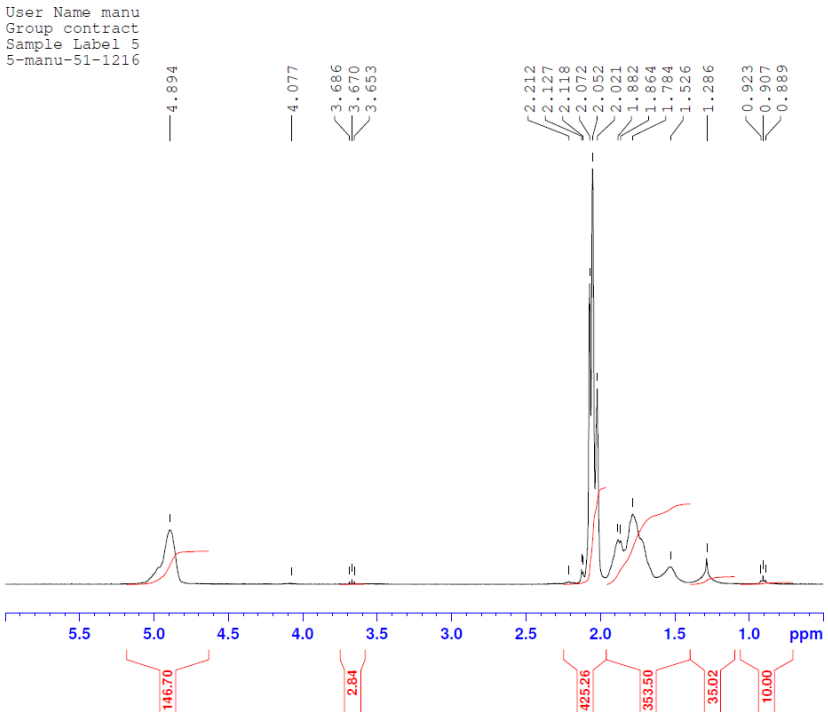
* Lo- Low pressure reactor. Experiment conducted at temperature of 60°C and agitation of 400 rpm.



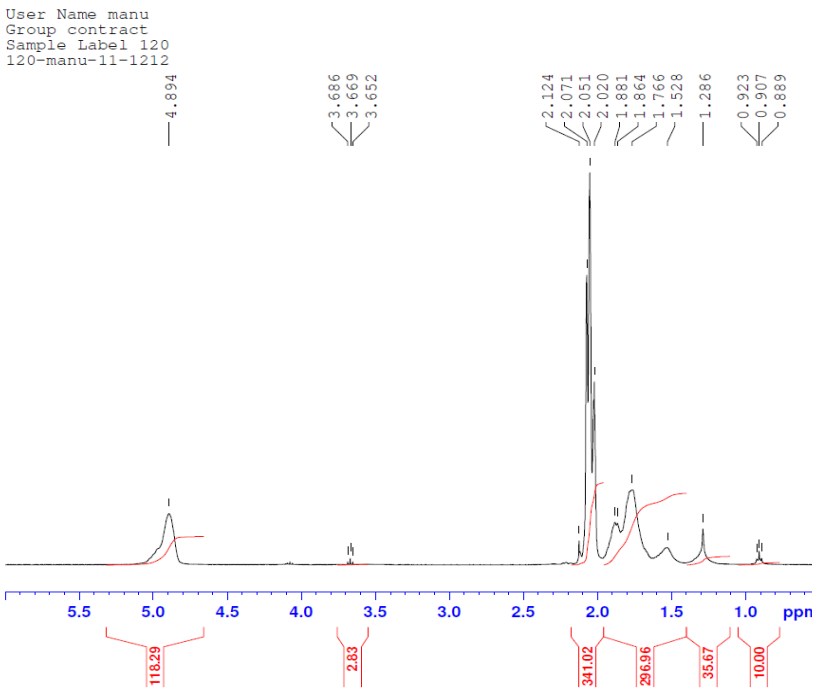
Time point (min)	VAc peak integral ($I_{0.8\text{-}2.3ppm}$)	Eth peak integral ($I_{4.9ppm}$)	Eth/VAc molar ratio in copolymer (mol/mol)
15	1523.69	266.80	0.178



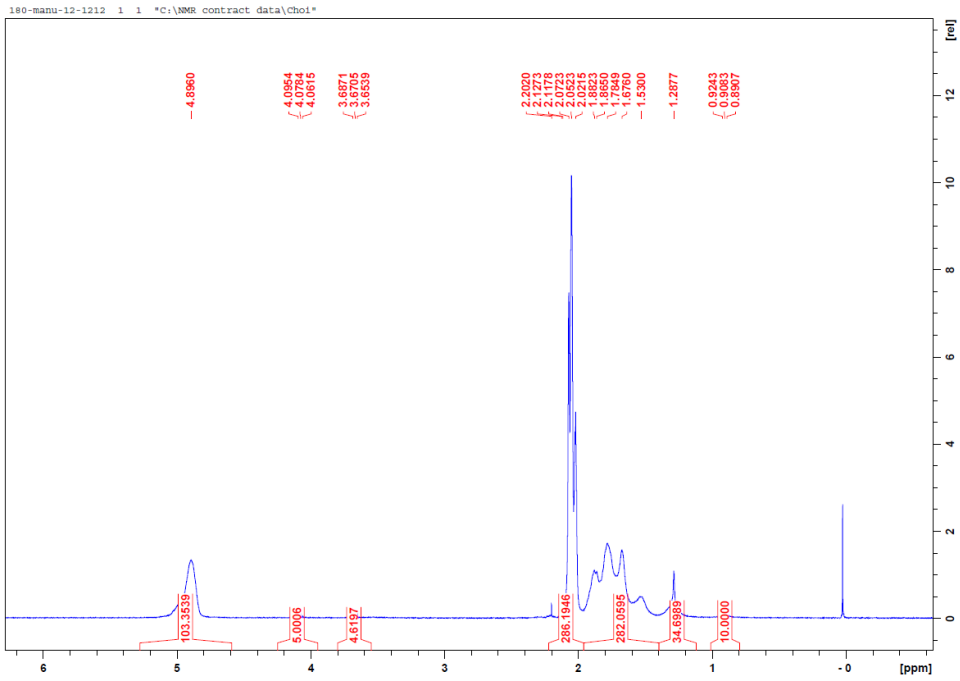
Time point (min)	VAc peak integral ($I_{0.8\text{-}2.3ppm}$)	Eth peak integral ($I_{4.9ppm}$)	Eth/VAc molar ratio in copolymer (mol/mol)
20	1235.07	216.93	0.173



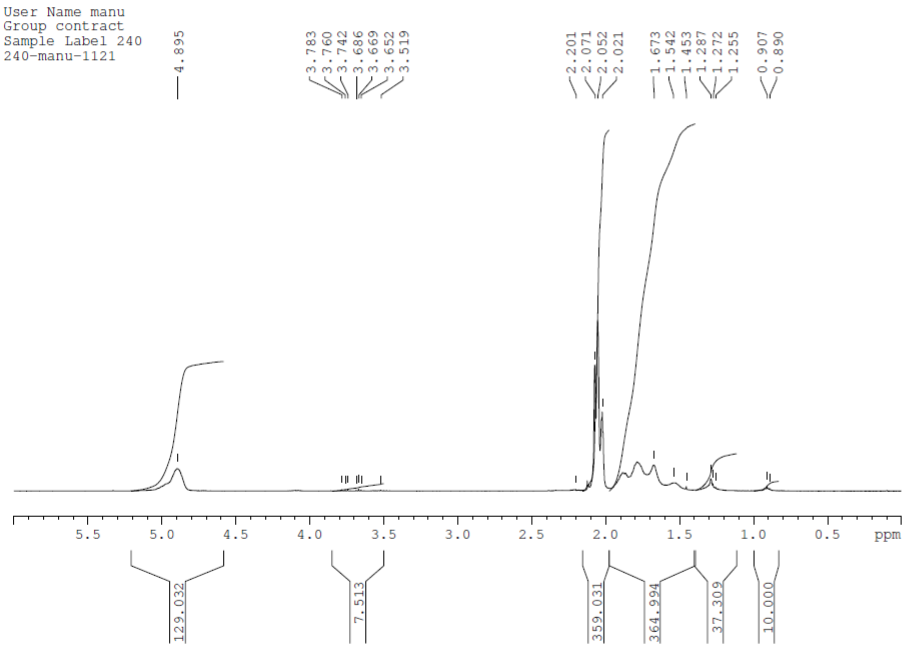
Time point (min)	VAc peak integral ($I_{0.8\text{-}2.3ppm}$)	Eth peak integral ($I_{4.9ppm}$)	Eth/VAc molar ratio in copolymer (mol/mol)
30	823.78	146.70	0.154



Time point (min)	VAc peak integral ($I_{0.8\text{-}2.3ppm}$)	Eth peak integral ($I_{4.9ppm}$)	Eth/VAc molar ratio in copolymer (mol/mol)
120	683.65	118.29	0.195



Time point (min)	VAc peak integral ($I_{0.8\text{-}2.3ppm}$)	Eth peak integral ($I_{4.9ppm}$)	Eth/VAc molar ratio in copolymer (mol/mol)
180	612.96	103.35	0.233

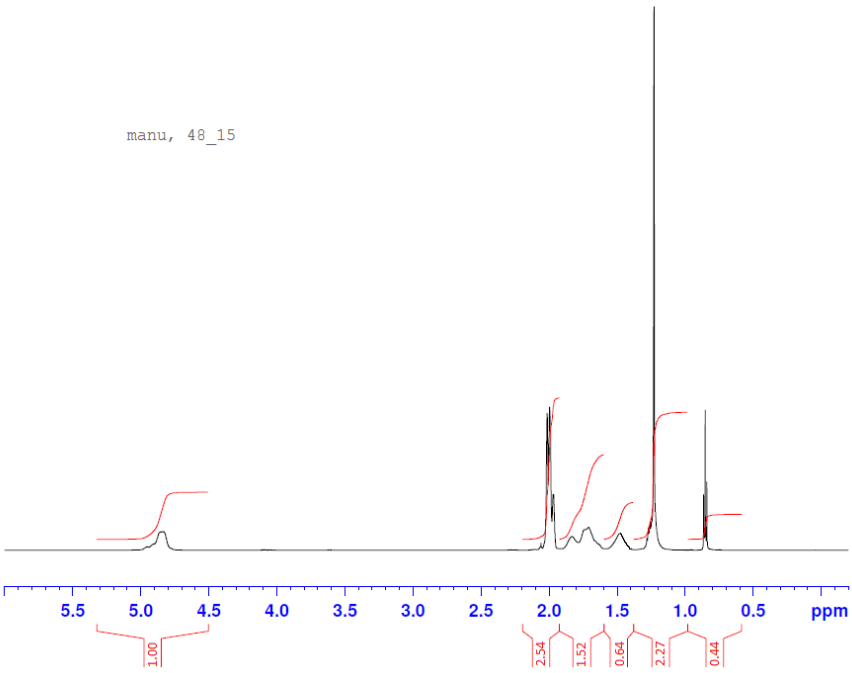


Time point (min)	VAc peak integral ($I_{0.8\text{-}2.3ppm}$)	Eth peak integral ($I_{4.9ppm}$)	Eth/VAc molar ratio in copolymer (mol/mol)
240	771.33	129.03	0.244

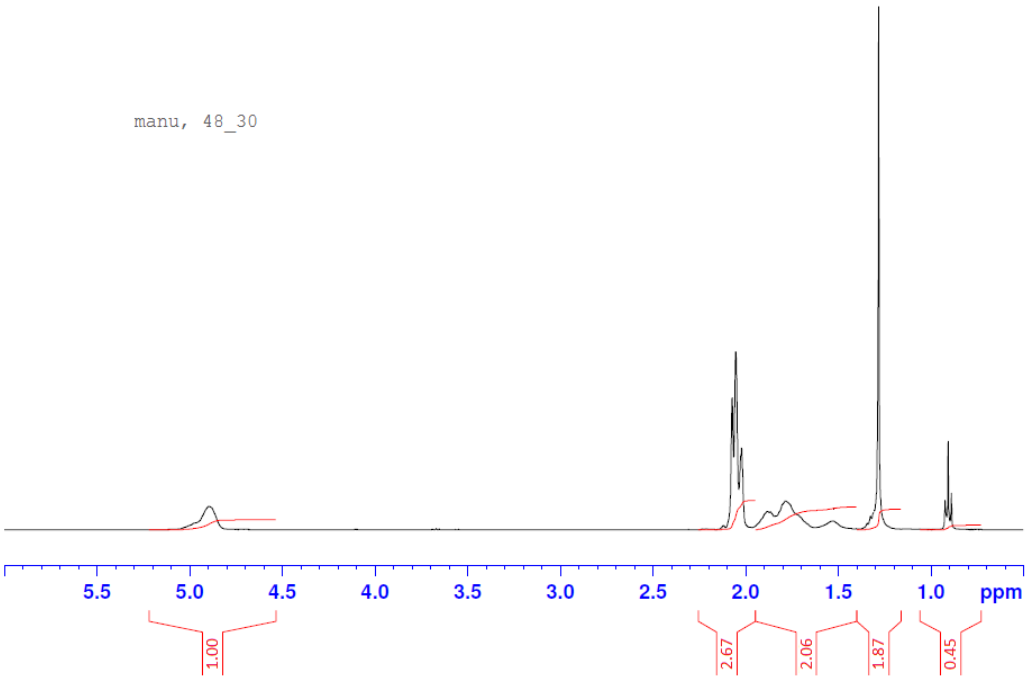
B.2. Miniemulsion run ME-VAE 48

Run no.	Emulsion type and reactor *		Water (mol)	VAc (mol)	Wt% VAc in monomer mixture (g-VAc/g-mixture)	SDS % (mol/mol VAc)	KPS % (mol/mol VAc)	HD %(mol/mol VAc)	Ethylene partial pressure (psig)
MU-VAE 48	U	Lo	8.33	0.33	0.159	1.16	0.50	7.05	80

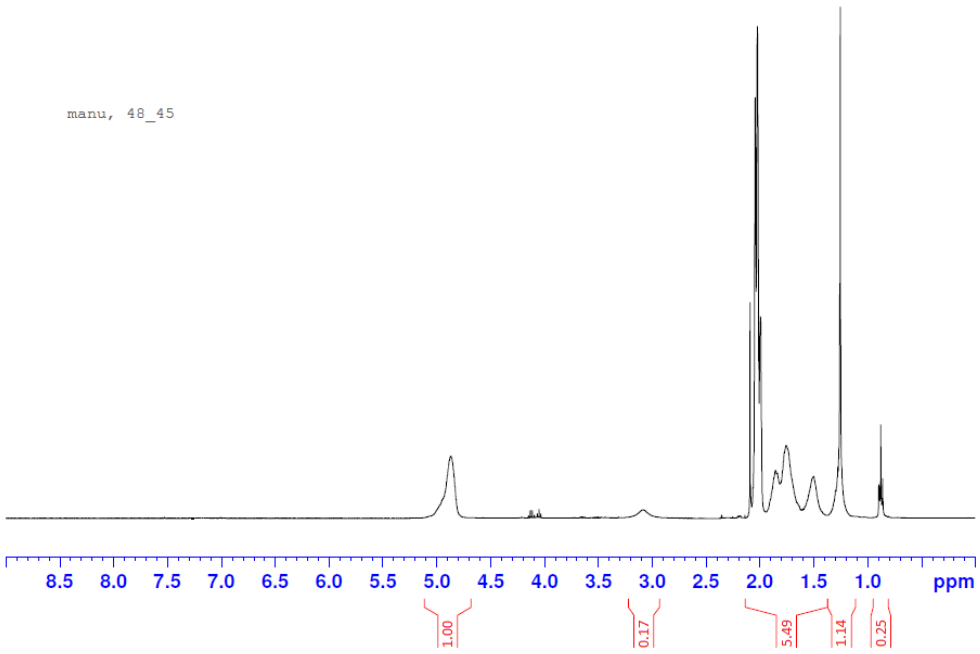
* U- Miniemulsion by ultrasonication, Lo- Low pressure reactor. Experiment conducted at temperature of 60°C and agitation of 700 rpm.



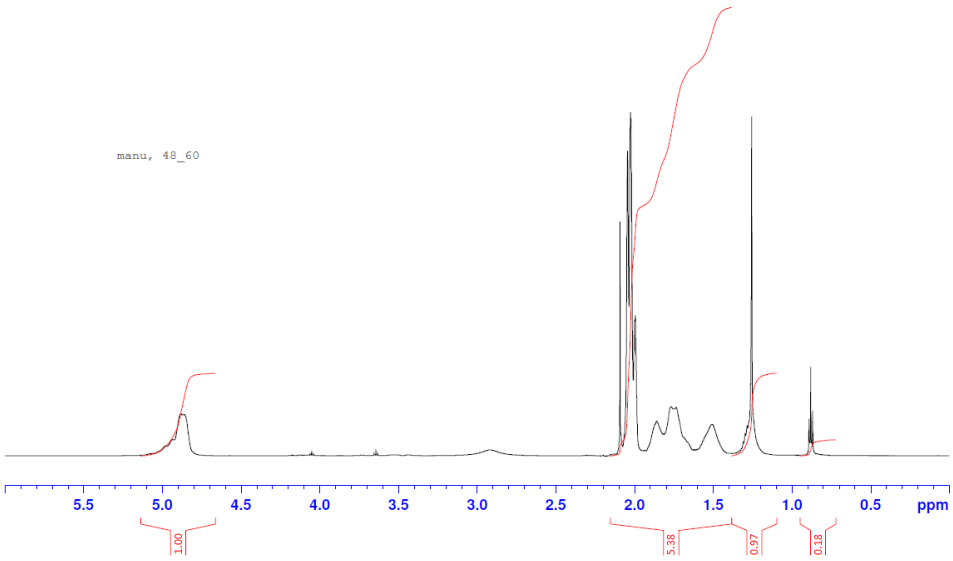
Time point (min)	VAc peak integral ($I_{0.8\text{-}2.3ppm}$)	Eth peak integral ($I_{4.9ppm}$)	Eth/VAc molar ratio in copolymer (mol/mol)
15	7.41	1.00	0.603



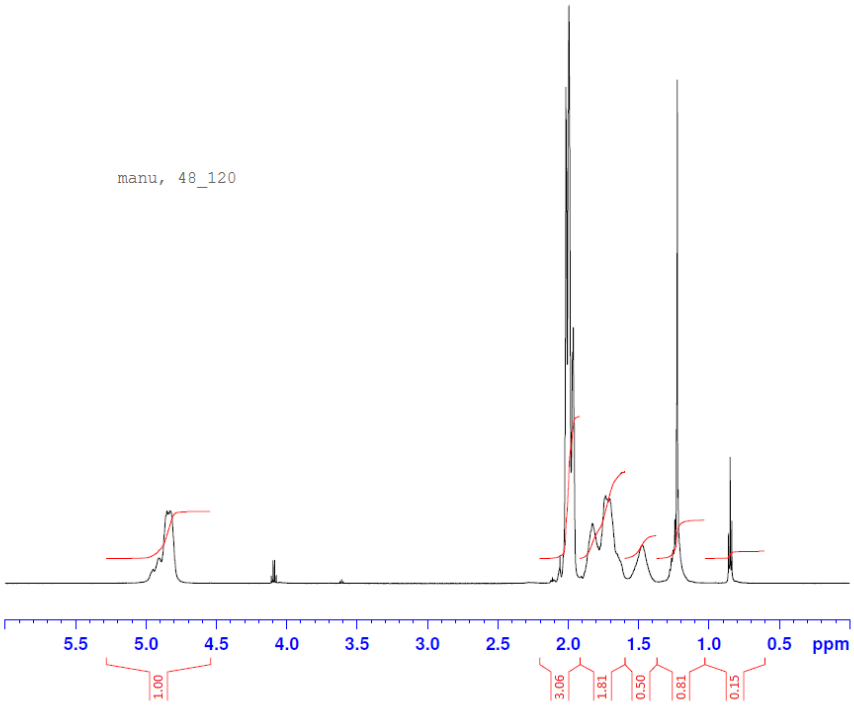
Time point (min)	VAc peak integral ($I_{0.8\text{-}2.3ppm}$)	Eth peak integral ($I_{4.9ppm}$)	Eth/VAc molar ratio in copolymer (mol/mol)
30	7.05	1.00	0.513



Time point (min)	VAc peak integral ($I_{0.8\text{-}2.3ppm}$)	Eth peak integral ($I_{4.9ppm}$)	Eth/VAc molar ratio in copolymer (mol/mol)
45	771.33	129.03	0.244

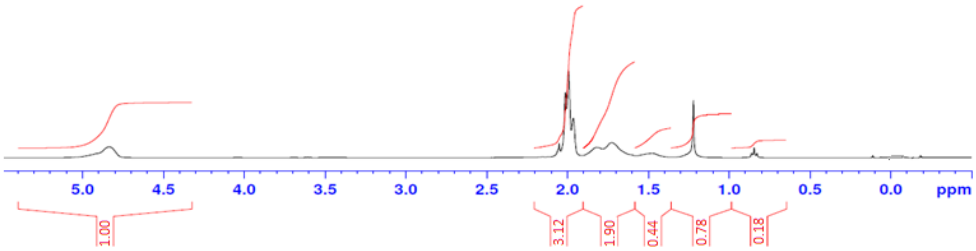


Time point (min)	VAc peak integral ($I_{0.8\text{-}2.3ppm}$)	Eth peak integral ($I_{4.9ppm}$)	Eth/VAc molar ratio in copolymer (mol/mol)
60	6.53	1.00	0.383



Time point (min)	VAc peak integral ($I_{0.8\text{-}2.3ppm}$)	Eth peak integral ($I_{4.9ppm}$)	Eth/VAc molar ratio in copolymer (mol/mol)
120	6.33	1.00	0.333

manu, 48_240



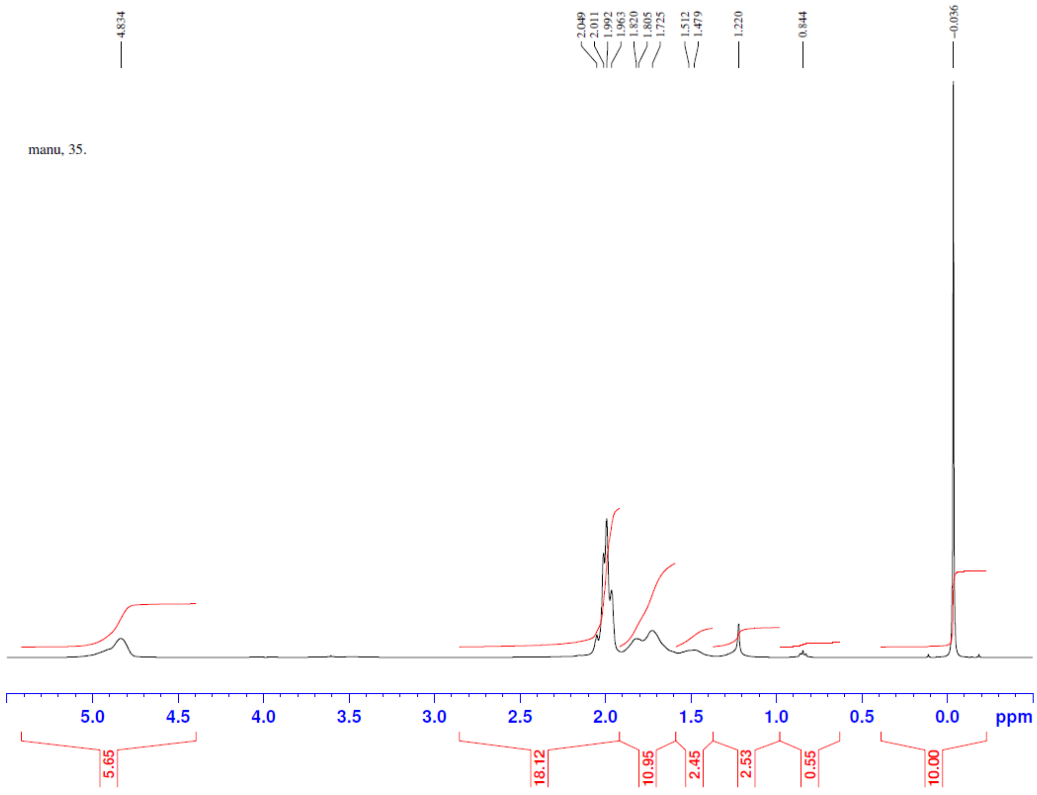
Time point (min)	VAc peak integral ($I_{0.8\text{-}2.3ppm}$)	Eth peak integral ($I_{4.9ppm}$)	Eth/VAc molar ratio in copolymer (mol/mol)
240	6.42	1.00	0.355

Appendix C. ^{1}H NMR data at different pressures for VAE emulsion and miniemulsion

Appendix C.1. High pressure VAE emulsion copolymerization runs

Run no.	Reactor type *	Water (mol)	VAc (mol)	Wt% VAc in monomer mixture (g-VAc/g-mixture)	SDS % (mol/mol VAc)	KPS % (mol/mol VAc)	Ethylene partial pressure (psig)
ME-VAE 35	Hi	21.11	0.76	0.147	0.97	0.31	100

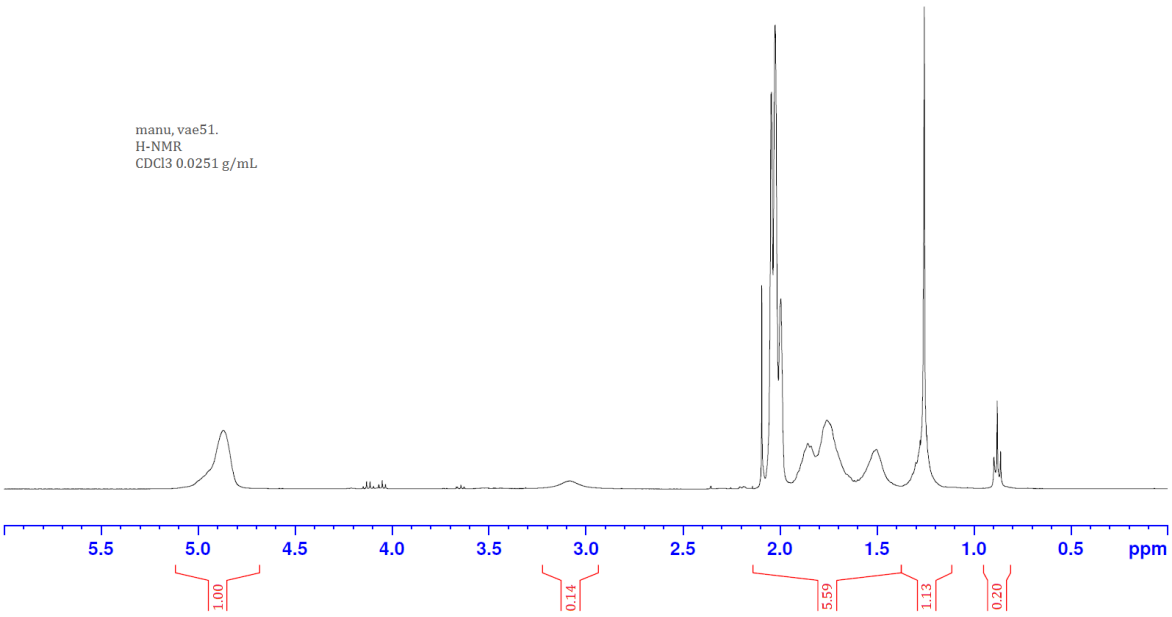
* Hi- High pressure reactor. Experiment conducted at temperature of 60°C and agitation of 700 rpm



VAc peak integral ($I_{0.8\text{-}2.3ppm}$)	Eth peak integral ($I_{4.9ppm}$)	Eth/VAc molar ratio in copolymer (mol/mol)
34.60	5.65	0.281

Run no.	Reactor type *	Water (mol)	VAc (mol)	Wt% VAc in monomer mixture (g-VAc/g-mixture)	SDS % (mol/mol VAc)	KPS % (mol/mol VAc)	Ethylene partial pressure (psig)
ME-VAE 51	Hi	21.11	0.76	0.147	0.97	0.31	150

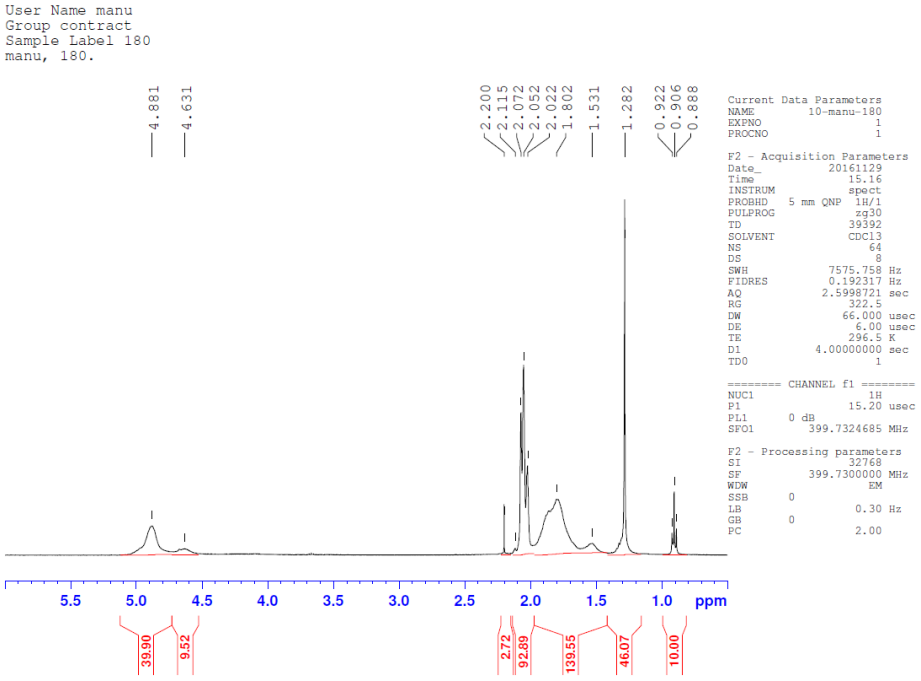
* Hi- High pressure reactor. Experiment conducted at temperature of 60°C and agitation of 700 rpm



VAc peak integral ($I_{0.8\text{-}2.3ppm}$)	Eth peak integral ($I_{4.9ppm}$)	Eth/VAc molar ratio in copolymer (mol/mol)
6.92	1.00	0.480

Run no.	Reactor type *	Water (mol)	VAc (mol)	Wt% VAc in monomer mixture (g-VAc/g-mixture)	SDS % (mol/mol VAc)	KPS % (mol/mol VAc)	Ethylene partial pressure (psig)
ME-VAE 37	Hi	21.11	0.76	0.147	0.97	0.31	200

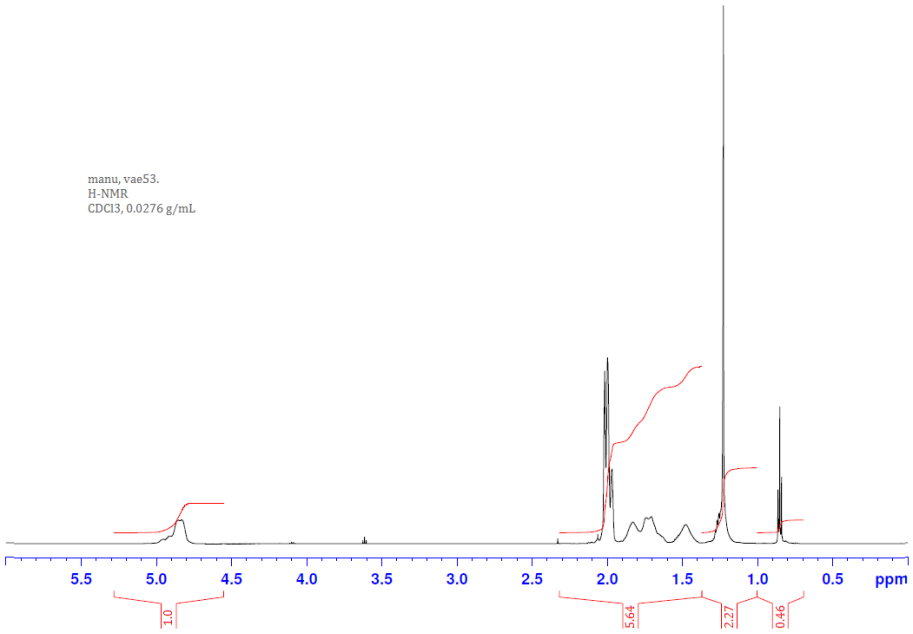
* Hi- High pressure reactor. Experiment conducted at temperature of 60°C and agitation of 700 rpm



VAc peak integral ($I_{0.8\text{-}2.3ppm}$)	Eth peak integral ($I_{4.9ppm}$)	Eth/VAc molar ratio in copolymer (mol/mol)
291.23	39.90	0.575

Run no.	Reactor type *	Water (mol)	VAc (mol)	Wt% VAc in monomer mixture (g-VAc/g-mixture)	SDS % (mol/mol VAc)	KPS % (mol/mol VAc)	Ethylene partial pressure (psig)
ME-VAE 53	Hi	21.11	0.76	0.147	0.97	0.31	250

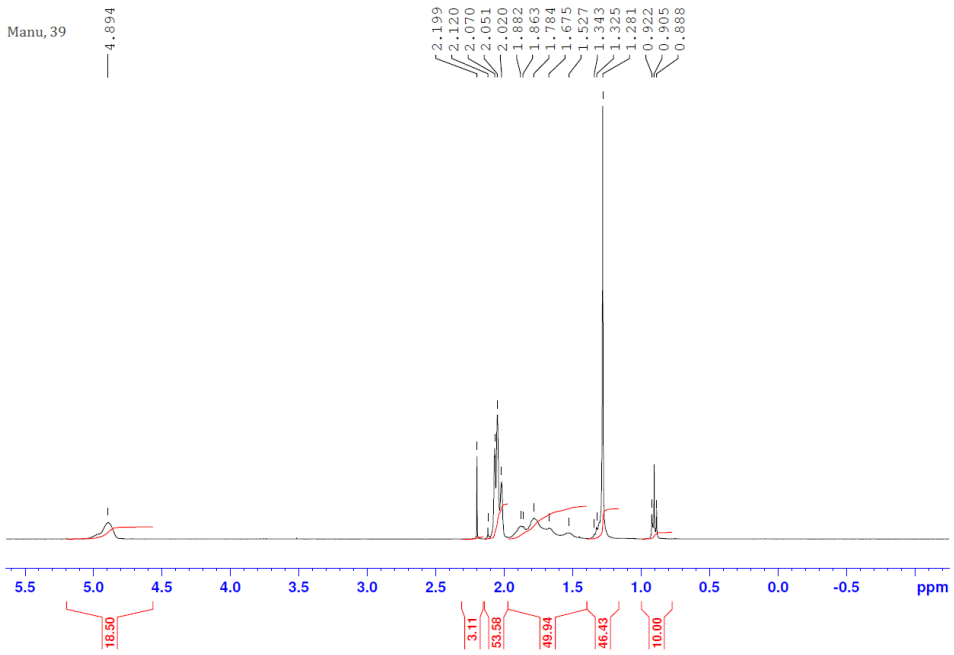
* Hi- High pressure reactor. Experiment conducted at temperature of 60°C and agitation of 700 rpm



VAc peak integral ($I_{0.8\text{-}2.3ppm}$)	Eth peak integral ($I_{4.9ppm}$)	Eth/VAc molar ratio in copolymer (mol/mol)
8.37	1.00	0.843

Run no.	Reactor type *	Water (mol)	VAc (mol)	Wt% VAc in monomer mixture (g-VAc/g-mixture)	SDS % (mol/mol VAc)	KPS % (mol/mol VAc)	Ethylene partial pressure (psig)
ME-VAE 39	Hi	21.11	0.76	0.147	0.92	0.31	300

* Hi- High pressure reactor. Experiment conducted at temperature of 60°C and agitation of 700 rpm

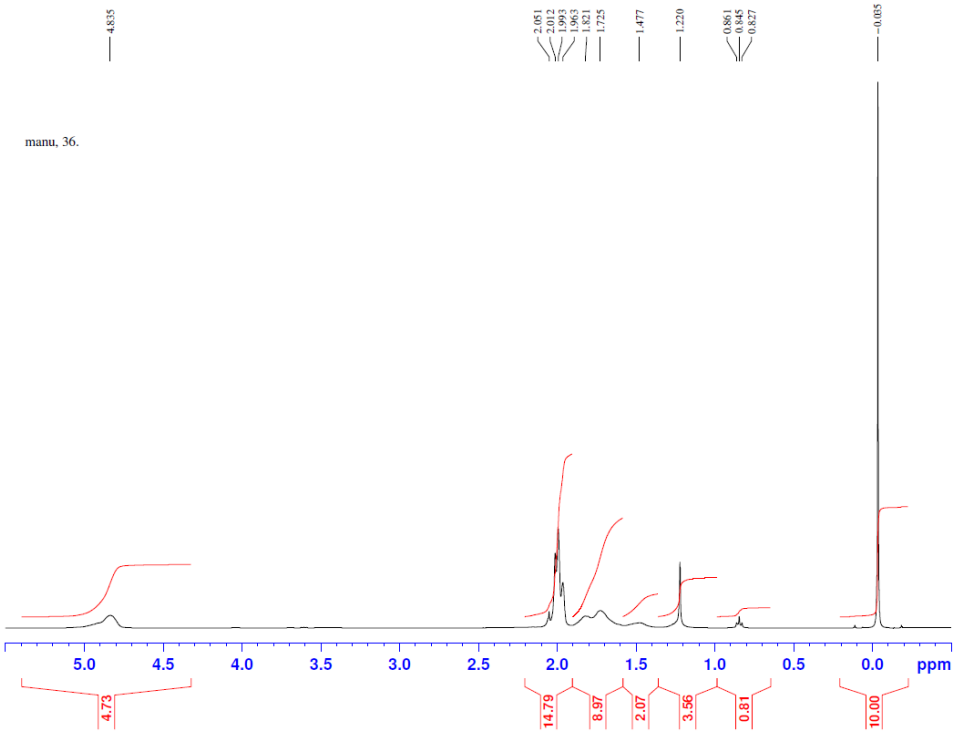


VAc peak integral ($I_{0.8\text{-}2.3ppm}$)	Eth peak integral ($I_{4.9ppm}$)	Eth/VAc molar ratio in copolymer (mol/mol)
163.06	18.50	0.954

Appendix C.2. High pressure VAE miniemulsion copolymerization runs

Run no.	Emulsion type and reactor *		Water (mol)	VAc (mol)	Wt% VAc in monomer mixture (g-VAc/g-mixture)	SDS % (mol/mol VAc)	KPS % (mol/mol VAc)	HD %(mol/mol VAc)	Ethylene partial pressure (psig)
MU-VAE 36	U	Hi	21.11	0.76	0.147	0.79	0.50	6.98	100

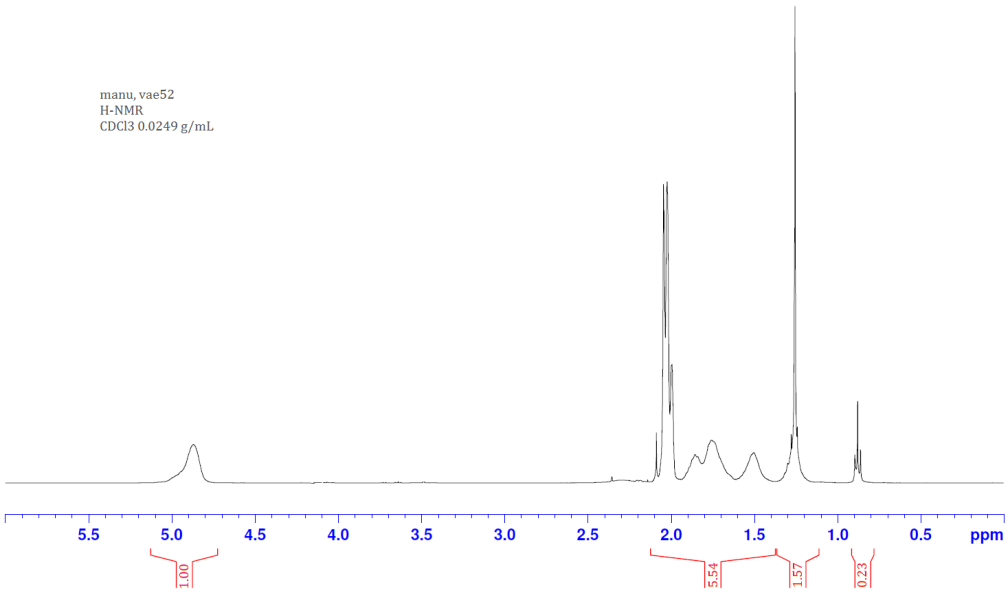
* U- Miniemulsion by ultrasonication, H- Miniemulsion by homogenization, Hi- High pressure reactor. Experiment conducted at temperature of 60°C and agitation of 700 rpm.



VAc peak integral ($I_{0.8\text{-}2.3ppm}$)	Eth peak integral ($I_{4.9ppm}$)	Eth/VAc molar ratio in copolymer (mol/mol)
30.20	4.73	0.346

Run no.	Emulsion type and reactor *		Water (mol)	VAc (mol)	Wt% VAc in monomer mixture (g-VAc/g-mixture)	SDS % (mol/mol VAc)	KPS % (mol/mol VAc)	HD %(mol/mol VAc)	Ethylene partial pressure (psig)
MU-VAE 52	U	Hi	21.11	0.76	0.147	0.78	0.50	6.98	150

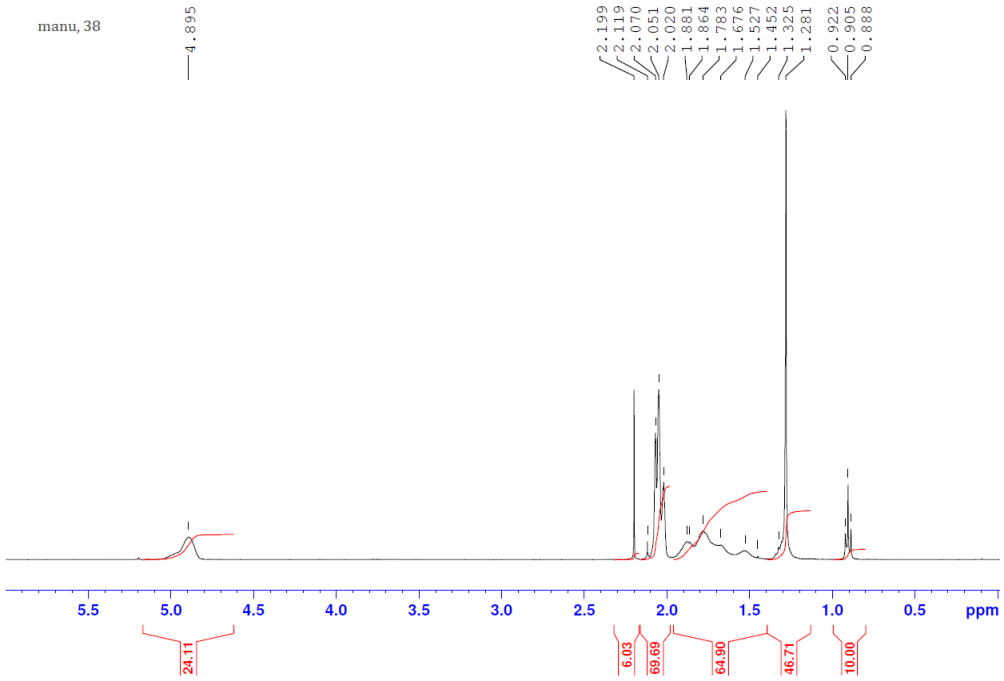
* U- Miniemulsion by ultrasonication, H- Miniemulsion by homogenization, Hi- High pressure reactor. Experiment conducted at temperature of 60°C and agitation of 700 rpm.



VAc peak integral ($I_{0.8\text{-}2.3ppm}$)	Eth peak integral ($I_{4.9ppm}$)	Eth/VAc molar ratio in copolymer (mol/mol)
7.34	1.00	0.585

Run no.	Emulsion type and reactor *		Water (mol)	VAc (mol)	Wt% VAc in monomer mixture (g-VAc/g-mixture)	SDS % (mol/mol VAc)	KPS % (mol/mol VAc)	HD %(mol/mol VAc)	Ethylene partial pressure (psig)
MU-VAE 38	U	Hi	21.11	0.76	0.147	0.79	0.50	6.98	200

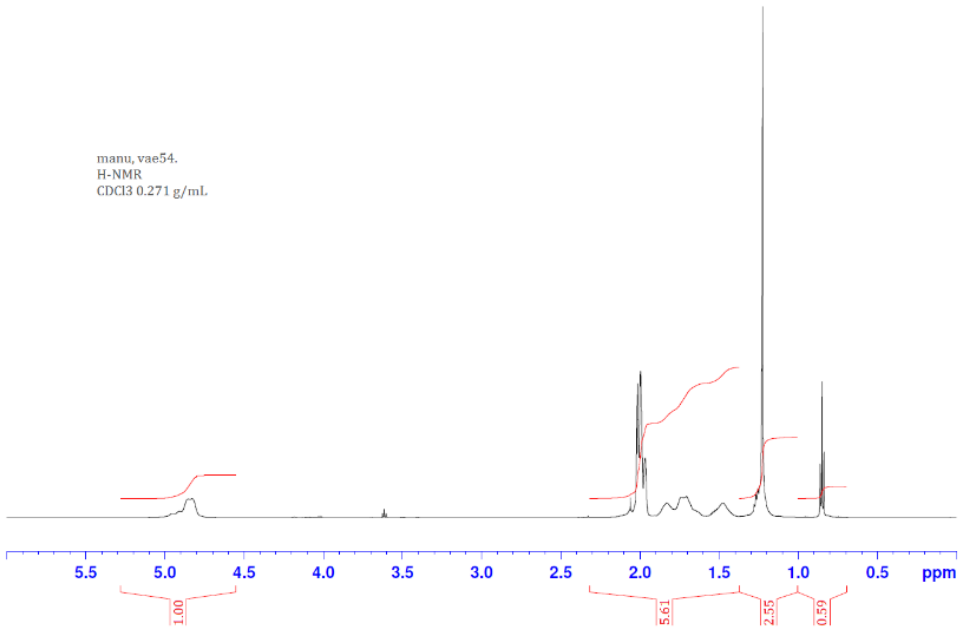
* U- Miniemulsion by ultrasonication, H- Miniemulsion by homogenization, Hi- High pressure reactor. Experiment conducted at temperature of 60°C and agitation of 700 rpm.



VAc peak integral ($I_{0.8\text{-}2.3ppm}$)	Eth peak integral ($I_{4.9ppm}$)	Eth/VAc molar ratio in copolymer (mol/mol)
197.33	24.11	0.796

Run no.	Emulsion type and reactor *		Water (mol)	VAc (mol)	Wt% VAc in monomer mixture (g-VAc/g-mixture)	SDS % (mol/mol VAc)	KPS % (mol/mol VAc)	HD %(mol/mol VAc)	Ethylene partial pressure (psig)
MU-VAE 54	U	Hi	21.11	0.76	0.147	0.78	0.50	6.98	250

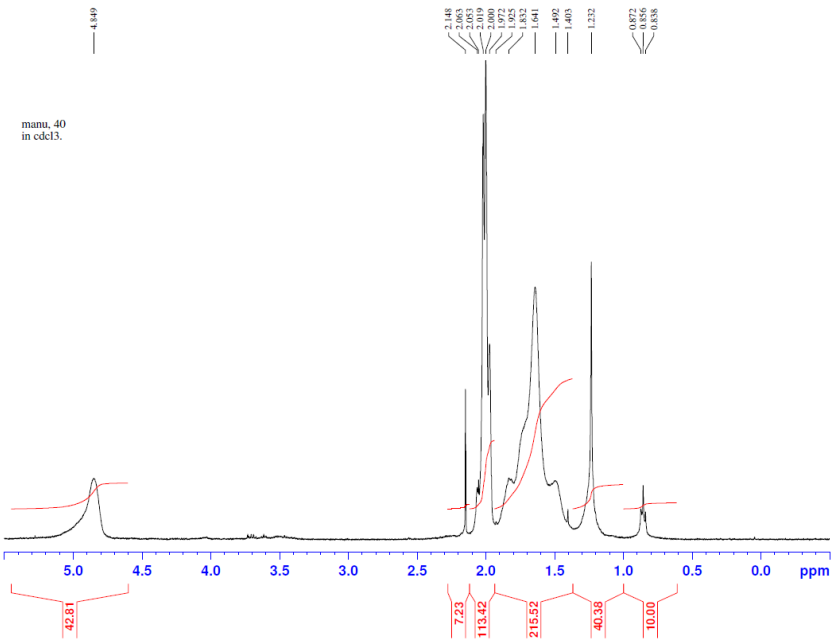
* U- Miniemulsion by ultrasonication, H- Miniemulsion by homogenization, Hi- High pressure reactor. Experiment conducted at temperature of 60°C and agitation of 700 rpm.



VAc peak integral ($I_{0.8\text{-}2.3ppm}$)	Eth peak integral ($I_{4.9ppm}$)	Eth/VAc molar ratio in copolymer (mol/mol)
8.75	1.00	0.938

Run no.	Emulsion type and reactor *		Water (mol)	VAc (mol)	Wt% VAc in monomer mixture (g-VAc/g-mixture)	SDS % (mol/mol VAc)	KPS % (mol/mol VAc)	HD %(mol/mol VAc)	Ethylene partial pressure (psig)
MU-VAE 40	U	Hi	21.11	0.76	0.147	0.78	0.50	6.98	300

* U- Miniemulsion by ultrasonication, H- Miniemulsion by homogenization, Hi- High pressure reactor. Experiment conducted at temperature of 60°C and agitation of 700 rpm.



VAc peak integral ($I_{0.8\text{-}2.3ppm}$)	Eth peak integral ($I_{4.9ppm}$)	Eth/VAc molar ratio in copolymer (mol/mol)
386.55	42.81	1.007

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TENTATIVE PUBLICATION

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